

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 July 2003 (31.07.2003)

PCT

(10) International Publication Number
WO 03/062298 A1

(51) International Patent Classification⁷: **C08G 63/00**,
63/02, 73/00, A61F 2/00

(21) International Application Number: PCT/US02/01258

(22) International Filing Date: 17 January 2002 (17.01.2002)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant: **POLYRAVA LLC** [US/US]; 23205 Mercantile Road, Beachwood, OH 44122 (US).

(72) Inventor: **KATSARAVA, Ramaz**; 1a Tskneti Street, Apartment 16, Tbilisi, 380062 (GE).

(74) Agent: **CRIMALDI, Joseph**; Renner, Otto, Boisselle & Sklar, LLP, 1621 Euclid Avenue, 19th Floor, Cleveland, OH 44115 (US).

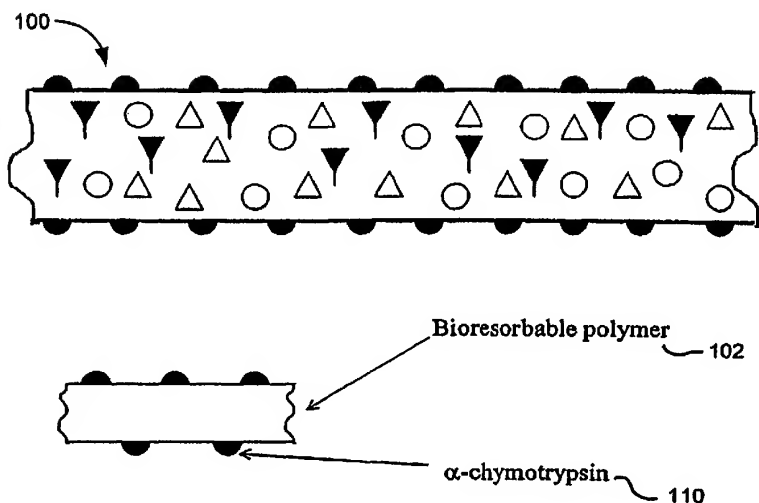
(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CO-POLY(ESTER AMIDE) AND CO-POLY(ESTER URETHANE) COMPOSITIONS WHICH EXHIBIT BIODEGRADABILITY, METHODS FOR MAKING SAME AND USES FOR SAME



(57) Abstract: The present invention relates to a polymeric compositions which can be used to form a variety of biodegradable objects and to methods for making the same. In particular, the present invention relates to polymers made from a combination of: (1) the combination of at least two di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester with at least one active diester; (2) the combination of at least two di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester with at least one active bis-carbonate of a diol; (3) the combination of at least one di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester and at least one di-p-toluenesulfonic acid salt of an ester (e.g., a diamino ester) with at least one active diester; and (4) the combination of at least one di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester and at least one di-p-toluenesulfonic acid salt of an ester (e.g., a diamino ester) with at least one active bis-carbonate of a diol. The present invention also relates to methods for making the above mentioned polymers and uses for same.

- ▼ - Bacteriophage ~ 104
○ - Antibiotic ~ 106
△ - Anesthetic ~ 108

**CO-POLY(ESTER AMIDE) AND CO-POLY(ESTER URETHANE)
COMPOSITIONS WHICH EXHIBIT BIODEGRADABILITY,
METHODS FOR MAKING SAME AND USES FOR SAME**

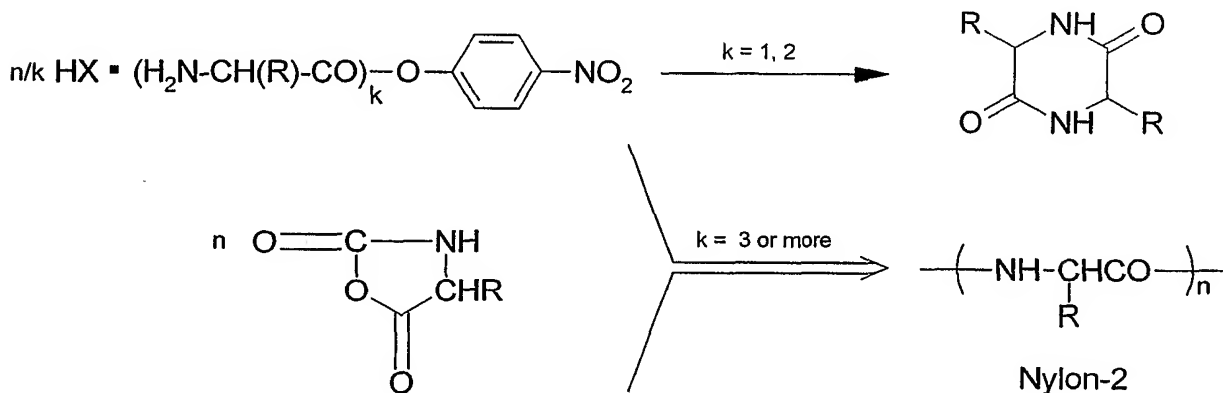
FIELD OF THE INVENTION

The invention described herein relates generally to polymeric compositions which can be used to form a variety of biodegradable objects and to methods for making the same. In particular, the present invention relates to polymers made from: (1) the combination of at least two di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester with at least one active diester; (2) the combination of at least two di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester with at least one active bis-carbonate of a diol; (3) the combination of at least one di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester and at least one di-p-toluenesulfonic acid salt of an ester (*e.g.*, a diamino ester) with at least one active diester; and (4) the combination of at least one di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester and at least one di-p-toluenesulfonic acid salt of an ester (*e.g.*, a diamino ester) with at least one active bis-carbonate of a diol. The present invention also relates to methods for making the above mentioned compounds and uses for same.

BACKGROUND OF THE INVENTION

Several polymers have been described in the art as being degradable, biodegradable, compostable, and the like. However, such polymers typically suffer from numerous limitations and/or drawbacks which detract from their utility in a number of applications. For example, conventional poly- α -amino acids (PAAs) are difficult and costly to manufacture via a ring-opening polymerization process which utilizes unstable and expensive N-carboxyanhydrides. One such process is shown below.

Further problems common to poly- α -amino acids formulated by the above process include insolubility in common organic solvents, susceptibility to thermal degradation during a melting process; rates of biodegradation that are too slow for biomedical engineering uses; and an increase in immunogenicity with increasing molecular complexity (e.g., increased branching) and the number of α -amino acid residues present in the copolymer.



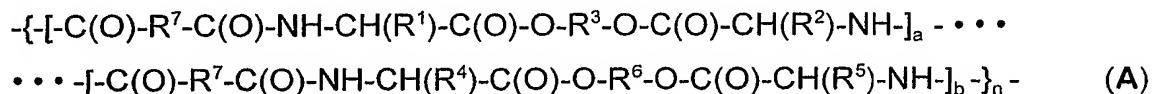
Thus, there is a need for degradable, biodegradable, and/or compostable polymers which are less expensive to produce, possess a wide range of chemical, biological and material properties, and are easy to process into a desired biodegradable object.

SUMMARY OF THE INVENTION

The present invention relates to polymers made using: (1) the combination of at least two di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester with at least one active diester; (2) the combination of at least two di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester with at least one active bis-carbonate of a diol; (3) the combination of at least one di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester and at least one di-p-toluenesulfonic acid salt of an ester (e.g., a diamino ester) with at least one active diester; and (4) the combination of at least one di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester and at least one di-p-toluenesulfonic

acid salt of an ester (e.g., a diamino ester) with at least one active bis-carbonate of a diol. Methods for making the above co-poly(ester amide)s and co-poly(ester urethane)s are also disclosed herein.

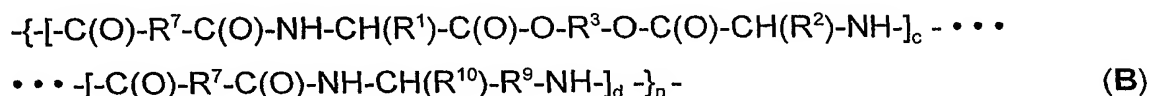
5 In accordance with one aspect of the invention, the present invention relates to co-poly(ester amide) compositions which contain at least two amino acid sub-components comprising repeating units according to the following formula:



10 where R^1 , R^2 , R^4 and R^5 are independently selected from $-CH_3$, $-CH_2CH_3$, linear and branched C_3 to C_{20} alkyl, C_2 to C_3 thioalkyl, linear or branched C_4 to C_{20} thioalkyl, $-CH_2-C_6H_5$, $-CH_2-CH_2-C_6H_5$, and linear and branched C_3 - C_{20} alkyl with at least one terminal phenyl group; R^3 and R^6 are independently selected from $-(CH_2)_x-$, where x is from 2 to about 40; R^7 is selected from $-(CH_2)_y-$, where y is from 2 to about 40; n is from about 20 to about 500; the ratio of a/b is in the range of about 90:10 to about 10:90; and at least one of R^1 , R^2 , R^3 or the first R^7 is different from at least one of R^4 , R^5 , R^6 or the second R^7 .

In accordance with another aspect of the invention, the at least two amino acid sub-components of Formula (A) are different.

20 In accordance with another aspect of the invention, the present invention relates to co-poly(ester amide) compositions which contain at least two amino acid sub-components comprising repeating units according to the following formula:



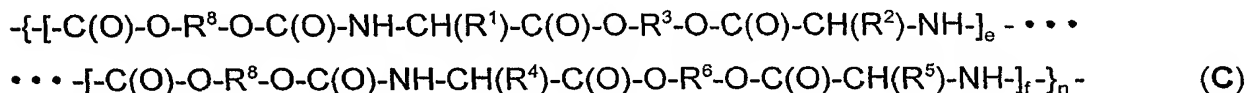
25 where R^1 and R^2 are independently selected from $-CH_3$, $-CH_2CH_3$, linear and branched C_3 to C_{20} alkyl, C_2 to C_3 thioalkyl, linear or branched C_4 to C_{20} thioalkyl, $-CH_2-C_6H_5$, $-CH_2-CH_2-C_6H_5$, and linear and branched C_3 - C_{20} alkyl with at least one terminal phenyl group; R^3 is selected from $-(CH_2)_x-$, where x is from 2 to about 40; R^7

is independently selected from $-(CH_2)_y-$, where y is from 2 to about 40; R^9 is selected from $-(CH_2)_r-$, where r is from 1 to about 40; R^{10} is selected from $-C(O)-O-C_mH_{2m+1}$ where m is 1 to about 60, and $-C(O)-O-R''$ where R'' is selected from hydrogen, $-CH_2-C_6H_5$, $-CH_2-CH_2-C_6H_5$, linear and branched C_3-C_{20} alkyl with at least one terminal phenyl group; n is about 10 to about 1,000; and the ratio of c/d is in the range of about 80:20 to about 20:80.

In accordance with another aspect of the invention, the at least two amino acid sub-components of Formula (B) are different.

In accordance with another aspect of invention, the first R^7 in Formula (B) is identical to the second R^7 in Formula (B).

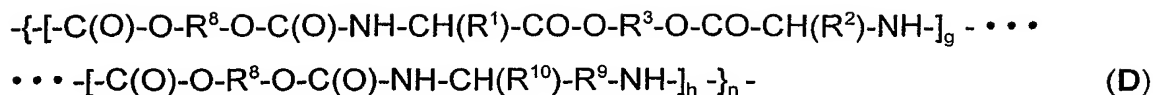
In accordance with another aspect of the invention, the present invention relates to co-poly(ester urethane) compositions which contain at least two amino acid sub-components comprising repeating units according to the following formula:



where R^1 , R^2 , R^4 and R^5 are independently selected from $-CH_3$, $-CH_2CH_3$, linear and branched C_3 to C_{20} alkyl, C_2 to C_3 thioalkyl, linear or branched C_4 to C_{20} thioalkyl, $-CH_2-C_6H_5$, $-CH_2-CH_2-C_6H_5$, and linear and branched C_3-C_{20} alkyl with at least one terminal phenyl group; R^3 and R^6 are independently selected from $-(CH_2)_x-$, where x is from 2 to about 40; R^8 is selected from $-(CH_2)_z-$, where z is from 2 to about 40, and $-(CH_2)_j-O-(CH_2)_k-$, where j and k are independently selected from 1 to about 20; n is about 10 to about 1,000; and the ratio of e/f is in the range of about 90:10 to about 10:90; and at least one of R^1 , R^2 , R^3 or the first R^8 is different from at least one of R^4 , R^5 , R^6 or the second R^8 .

In accordance with another aspect of the invention, the at least two amino acid sub-components of Formula (C) are different.

In accordance with another aspect of the invention, the present invention relates to co-poly(ester urethane) compositions which contain at least two amino acid sub-components comprising repeating units according to the following formula:

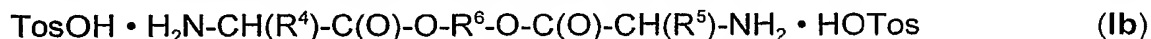
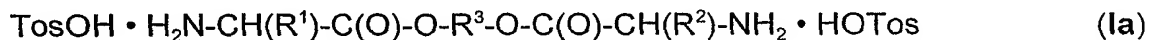


where R¹ and R² are independently selected from -CH₃, -CH₂CH₃, linear and branched C₃ to C₂₀ alkyl, C₂ to C₃ thioalkyl, linear or branched C₄ to C₂₀ thioalkyl, -CH₂-C₆H₅, -CH₂-CH₂-C₆H₅, and linear and branched C₃-C₂₀ alkyl with at least one terminal phenyl group; R³ is selected from -(CH₂)_x-, where x is from 2 to about 40; each R⁸ is independently selected from -(CH₂)_z-, where z is from 2 to about 40, and -(CH₂)_j-O-(CH₂)_k-, where j and k are independently selected from 1 to about 20; R⁹ is selected from -(CH₂)_r-, where r is from 1 to about 40; R¹⁰ is selected from -C(O)-O-C_mH_{2m+1} where m is 1 to about 60, and -C(O)-O-R" where R" is selected from hydrogen, -CH₂-C₆H₅, -CH₂-CH₂-C₆H₅, linear and branched C₃-C₂₀ alkyl with at least one terminal phenyl group; n is about 10 to about 1,000; and the ratio of g/h is in the range of about 80:20 to about 20:80.

In accordance with another aspect of the invention, the at least two amino acid sub-components of Formula (D) are different.

In accordance with another aspect of invention, the first R⁸ in Formula (D) is identical to the second R⁸ in Formula (D).

In accordance with another aspect of the invention, the present invention relates to a method for producing biodegradable polymers comprising the steps of: (A) combining at least one di-p-toluenesulfonic acid salt of a bis-(α-amino acid) α,ω-alkylene diesters according to Formulas (Ia) and/or (Ib) and optionally at least one di-p-toluenesulfonic acid salt of an ester according to Formula (IV) with at least one active diester according to Formula (II) or at least one active bis-carbonate of a diol according to Formula (III):



where R^1 , R^2 , R^4 and R^5 are independently selected from $-CH_3$, $-CH_2CH_3$, linear and branched C_3 to C_{20} alkyl, C_2 to C_3 thioalkyl, linear or branched C_4 to C_{20} thioalkyl, $-CH_2-C_6H_5$, $-CH_2-CH_2-C_6H_5$, and linear and branched C_3 - C_{20} alkyl with at least one terminal phenyl group; R^3 and R^6 are independently selected from $-(CH_2)_x-$, where x is from 2 to about 40; R^7 is selected from $-(CH_2)_y-$, where y is from 2 to about 40; X is $-O-C_6H_4-NO_2$; R^8 is selected from $-(CH_2)_z-$, where z is from 2 to about 40, and $-(CH_2)_j-O-(CH_2)_k-$, where j and k are independently selected from 1 to about 20; R^9 is selected from $-(CH_2)_r-$, where r is from 2 to about 40; and R^{10} is selected from $-C(O)-O-C_mH_{2m+1}$, where m is 1 to about 60, and $-C(O)-O-R''$ where R'' is selected from hydrogen, $-CH_2-C_6H_5$, $-CH_2-CH_2-C_6H_5$, linear and branched C_3 - C_{20} alkyl with at least one terminal phenyl group; (B) adding a tertiary amine initiator to the mixture of (A); (C) mixing the mixture of (B) at room temperature while increasing the temperature of the mixture to a temperature in the range of about 60 °C to about 120 °C; (D) subjecting the mixture of (B) to mixing at the final temperature of (C) for about 8 to about 16 hours; and (E) separating the polymer from the reaction by-products to yield a polymer product.

In accordance with another aspect of the invention, the present invention relates to a method for producing biodegradable polymers using a combination in step (A) of one diester according to Formula (Ia), one diester according to Formula (Ib) and one active diester according to Formula (II), wherein at least one of R^1 , R^2 or R^3 is different from at least one of R^4 , R^5 or R^6 .

In accordance with another aspect of the invention, the present invention relates to a method for producing biodegradable polymers using a combination in step (A) of one diester according to Formula (Ia) or (Ib) and two active diesters according to Formula (II), wherein the R^7 groups in the active diesters according to Formula (II) are different.

In accordance with another aspect of the invention, the present invention relates to a method for producing biodegradable polymers using a combination in step (A) of one diester according to Formula (Ia) or (Ib), one diester according to Formula (IV) and one active diester according to Formula (II).

In accordance with another aspect of the invention, the present invention relates to a method for producing biodegradable polymers using a combination in step (A) of one diester according to Formula (Ia), one diester according to Formula (Ib) and one active bis-carbonate according to Formula (III), wherein at least one of R¹, R² or R³ is different from at least one of R⁴, R⁵ or R⁶.

In accordance with another aspect of the invention, the present invention relates to a method for producing biodegradable polymers using a combination in step (A) of one diester according to Formula (Ia) or (Ib) and two active bis-carbonates according to Formula (III), wherein the R⁸ groups in the active diesters according to Formula (III) are different.

In accordance with another aspect of the invention, the present invention relates to a method for producing biodegradable polymers using a combination in step (A) of one diester according to Formula (Ia) or (Ib), one diester according to Formula (IV) and one active bis-carbonate according to Formula (III).

The foregoing compositions and/or methods provide any number of advantages. For example, the present biodegradable compositions and methods for providing the same are cost effective. Additionally, the present invention provides both biodegradable polymers and methods for making the same which have a variety of desirable chemical, biological and/or mechanical properties. Furthermore, the amino acid based bioanalogous polymers yielded by the reactions of the present invention are easy to process using solution casting (using, for example, common organic solvents) and/or melt casting techniques.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described and particularly pointed out in the claims. These embodiments are indicative, however, of but a few of the various ways in which the principles of the invention may be employed.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates wound covering formed using a polymer according to the present invention;

Figure 2 summarizes a method by which to produce polymers films from a polymer according to the present invention; and

Figure 3 illustrates the function of the various portions of the wound covering of Figure 1.

5

DETAILED DESCRIPTION OF THE INVENTION

The present invention involves a method for producing a variety of amino acid based bioanalogous polymers made from derivatives of α -amino acids and/or other nontoxic compounds. In particular, the present invention relates to co-poly(ester amide)s made using: (1) the combination of at least two di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester with at least one active diester; and
10 (2) the combination of at least one di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester and at least one di-p-toluenesulfonic acid salt of an ester (e.g., a diamino ester) with at least one active diester; and also to co-poly(ester urethane)s made using: (3) the combination of at least two di-p-toluenesulfonic acid
15 salts of a bis-(α -amino acid) α,ω -alkylene diester with at least one active bis-carbonate of a diol; and (4) the combination of at least one di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester and at least one di-p-toluenesulfonic acid salt of an ester (e.g., a diamino ester) with at least one active bis-carbonate of a diol. Methods for making the above co-poly(ester amide)s and
20 co-poly(ester urethane)s are also disclosed herein.

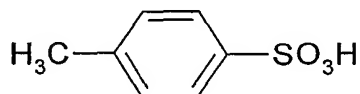
The present inventive compositions, and methods to produce the same, yield polymers which can be used to produce a wide range of biodegradable objects including, but not limited to, sutures, scaffolds (be they medical or otherwise), ligating clips and staples, surgical tubes or catheters, orthopedic implants, barriers to
25 prevent tissue adhesion, vascular grafts, stent coatings (medicated or non-medicated), artificial skin (medicated or non-medicated), bone substitutes, self-reinforced composites, temporary templates for cell growth, temporary contraceptives (e.g., stoppers for closing a fallopian tube, etc.), tampons,

biodegradable time release patches (e.g., patches for use with one or more drugs, physiologically active substances and bactericides) and artificial glands for releasing bio-active peptides and/or proteins.

Additionally, the present invention provides both biodegradable polymers and methods for making the same which have a variety of desirable chemical, biological and/or mechanical properties. Furthermore, the amino acid based bioanalogous polymers obtained by the reactions of the present invention are easy to process using solution casting (using, for example, common organic solvents) and/or melt casting techniques.

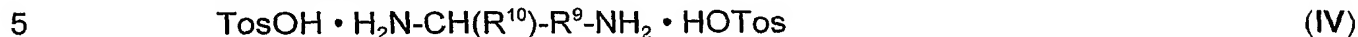
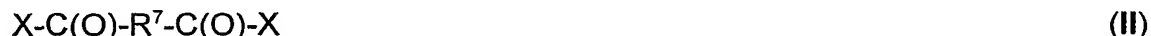
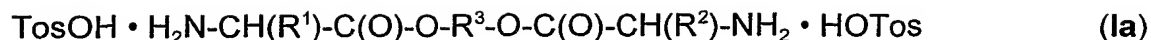
It should be noted that in the following text and claims, range and ratio limits and/or range and time limits may be combined. As used throughout the text and claims "biodegradable", "biodegradability", "biodegradation" and the like means the capability of undergoing natural processes in which a material is broken down by metabolic processes of living organisms (e.g., humans, other mammals or animals, fungi, bacteria, etc.). In the presence of oxygen (aerobic biodegradation), these metabolic processes yield carbon dioxide, water, biomass, and minerals. Under anaerobic conditions (anaerobic biodegradation), methane may additionally be produced.

Additionally, as used throughout the text and claims room temperature means a temperature in the range of about 20 °C to about 27 °C, and an amino acid means any naturally occurring or artificially produced amino acid. Also, TosOH is shorthand for the following formula:



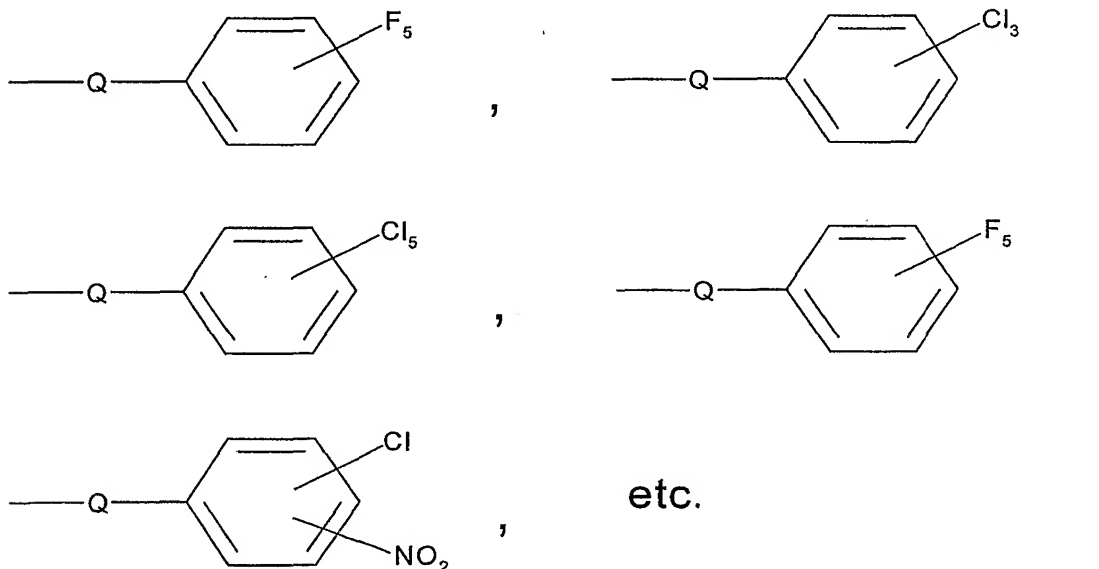
Co-Poly(ester amide)s and Co-Poly(ester urethane)s:

The present invention relates to co-poly(ester amide)s and co-poly(ester urethane)s made from various combinations, as will be explained below, of Formulas (Ia), (Ib), (II), (III) and (IV).

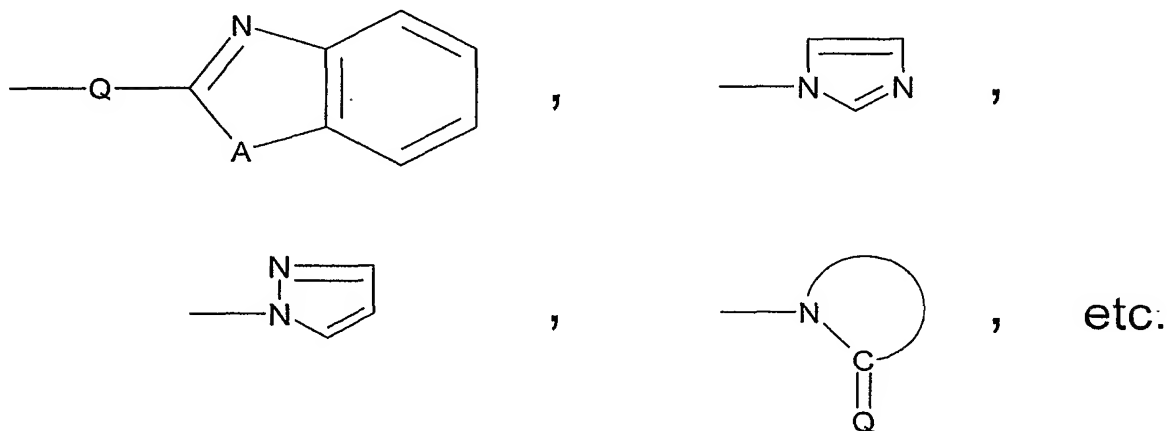


where R¹, R², R⁴ and R⁵ are independently selected from -CH₃, -CH₂CH₃, linear and branched C₃ to C₂₀ alkyl, C₂ to C₃ thioalkyl (e.g., -CH₂-S-CH₃, -CH₂-S-CH₂-CH₃, and -CH₂-CH₂-S-CH₃), linear or branched C₄ to C₂₀ thioalkyl, -CH₂-C₆H₅, -CH₂-CH₂-C₆H₅, and linear and branched C₃-C₂₀ alkyl with at least one terminal phenyl (-C₆H₅) group; R³ and R⁶ are independently selected from -(CH₂)_x-, where x is from 2 to about 40; R⁷ is selected from -(CH₂)_y-, where y is from 2 to about 40; R⁸ is selected from -(CH₂)_z-, where z is from 2 to about 40, and -(CH₂)_j-O-(CH₂)_k-, where j and k are independently selected from 1 to about 20; R⁹ is selected from -(CH₂)_r-, where r is from 1 to about 40; and R¹⁰ is selected from -C(O)-O-C_mH_{2m+1}, where m is 1 to about 60, and -C(O)-O-R" where R" is selected from hydrogen, -CH₂-C₆H₅, -CH₂-CH₂-C₆H₅, linear and branched C₃-C₂₀ alkyl with at least one terminal phenyl (-C₆H₅) group.

With regard to X, X is selected from -O-C₆H₄-NO₂, phenols or thiophenols with one more electron-withdrawing substituents (e.g., one or more of F, Cl, Br, NO₂, CN, etc.) such as, but not limited to, those groups shown below:



where Q is selected from O or S. X can also be selected from benzazols, imidazols, pyrazols, lactams or thiolactams groups. Exemplary structures for such groups are shown below. It should be noted that X is not limited to the structures of the groups shown above, rather X can be any group having the same basic chemical structure as those shown either above or below. For example,



where Q is selected from O or S, and A is selected from NH, O or S.

It should be noted that at least one of R^1 , R^2 or R^3 is different from at least one of R^4 , R^5 or R^6 (i.e., (Ia) is different from (Ib)) in order for there to be present two different di-p-toluenesulfonic acid salts of a bis-(α -amino acid) α,ω -alkylene diester in the reaction mixture.

In another embodiment, when two or more active diesters according to Formula (II) are utilized in the reaction mixture, the active diesters differ in that each active diester has a different R^7 group. In another embodiment, when two or more active bis-carbonates according to Formula (III) are utilized in the reaction mixture, the active bis-carbonates differ in that each active bis-carbonates has a different R^8 group.

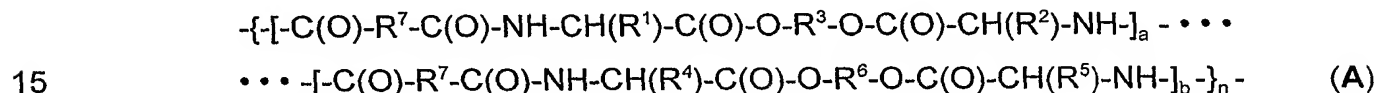
In another embodiment, R^1 , R^2 , R^4 and R^5 are independently selected from $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, linear and branched C_3 to C_6 alkyl, $-\text{CH}_2\text{CH}_2\text{S-CH}_3$, and $-\text{CH}_2\text{-C}_6\text{H}_5$. In yet another embodiment, R^3 and R^6 are independently selected from $-(\text{CH}_2)_x-$, where x is from 2 to about 20, even where x is from 2 to about 12. In still another embodiment, R^7 is selected from $-(\text{CH}_2)_y-$, where y is from 2 to about 30, even where y is from 2 to about 20. In still another embodiment, R^8 is selected from $-(\text{CH}_2)_z-$,

where z is from 2 to about 20, even where z is from 2 about 12, and
 $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$. In still another embodiment, R^9 is selected from $-(\text{CH}_2)_r-$, where r
 is from 2 to about 10, even where r is from 2 to about 6, or even where r is 4. In still
 another embodiment, R'' is selected from hydrogen, $-\text{CH}_2-\text{C}_6\text{H}_5$, and

5 $-\text{C}(\text{O})-\text{O}-\text{C}_m\text{H}_{2m+1}$ where m is 1 to about 40, even where m is 4, 8, 12, 16 or 20.

Co-Poly(ester amide)s

In one embodiment, the present invention relates to co-poly(ester amide)s
 according to Formula (A) made from the combination of at least two different di-p-
 toluenesulfonic acid salts of bis-(α -amino acid) α,ω -alkylene diester according to
 10 Formulas (Ia) and (Ib) and at least one active diester according to Formula (II). The
 above compounds are reacted using a suitable polymerization reaction (e.g., a
 polycondensation reaction) to yield co-poly(ester amide) polymers according to
 Formula (A) below:

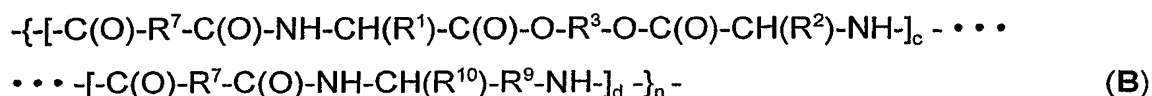


where R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are as defined above; n is from about 10 to
 about 1000 and the ratio of a/b is in the range of about 90:10 to about 10:90. In
 another embodiment, the ratio of a/b is from about 75:25 to about 25:75; or even
 from about 60:40 to about 40:60. In another embodiment, n is from about 20 to
 20 about 500, or even from about 30 to about 300.

In one embodiment, the polymers according to Formula (A) have a Mw of
 about 5,000 to about 400,000 daltons. In another embodiment, the polymers
 according to Formula (A) have a Mw of about 10,000 to about 200,000 daltons, even
 about 20,000 to about 100,000 daltons.

25 In another embodiment, when two active diesters according to Formula (II)
 are reacted with two different di-p-toluenesulfonic acid salts of bis-(α -amino acid)
 α,ω -alkylene diester according to Formulas (Ia) and (Ib) the polymers produced
 thereby have a formula according to Formula (A) above except that the first R^7
 group and the second R^7 group are different from one another.

In still another embodiment, the present invention relates to co-poly(ester amide)s according to Formula (B) made from the combination of at least one di-p-toluenesulfonic acid salt of a bis-(α -amino acid) α,ω -alkylene diester according to Formula (Ia) and/or (Ib), at least one di-p-toluenesulfonic acid salt of an ester according to Formula (IV) and at least one active diester according to Formula (II). In the discussion below Formula (Ia) is used. However, Formula (Ib) can be substituted for Formula (Ia) by changing the appropriate R groups in Formula (Ia) to match those contained in Formula (Ib). The above compounds are reacted using a suitable polymerization reaction (e.g., a polycondensation reaction) to yield co-poly(ester amide) polymers according to Formula (B) below:



where R^1 , R^2 , R^3 , R^7 , R^9 and R^{10} are as defined above n is from about 10 to about 1000 and the ratio of c/d is in the range of about 80:20 to about 20:80. In another embodiment, the ratio of c/d is from about 70:30 to about 30:70; or even from about 60:40 to about 40:60. In another embodiment, n is from about 20 to about 500, or even from about 30 to about 300.

In one embodiment, the polymers according to Formula (B) have a Mw of about 5,000 to about 400,000 daltons. In another embodiment, the polymers according to Formula (B) have a Mw of about 10,000 to about 200,000 daltons, even about 205,000 to about 100,000 daltons.

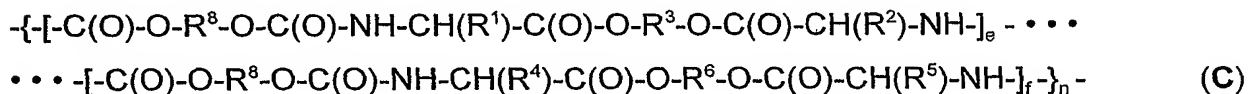
In another embodiment, when two active diesters according to Formula (II) are reacted with a di-p-toluenesulfonic acid salt of a bis-(α -amino acid) α,ω -alkylene diester according to Formula (Ia) or (Ib), and a di-p-toluenesulfonic acid salt of an ester according to Formula (IV), the polymers produced thereby have a formula according to Formula (B) above except that the first R^7 group and the second R^7 group are different from one another. This situation occurs when one active diester according to Formula (II) is pre-reacted with a di-p-toluenesulfonic acid salt of a bis-(α -amino acid) α,ω -alkylene diester according to Formula (Ia) or (Ib) and then the

second active diester according to Formula (II) and the a di-p-toluenesulfonic acid salt of an ester according to Formula (IV) are added to the product of the pre-reaction and the combination is further reacted. In another embodiment, if all four compounds are combined together and reacted simultaneously, this combination can yield a co-poly(ester amide) having four different repeating units.

In yet still another embodiment, the copolymers according to Formulas (A) and (B) contain three or more different repeating units rather than just two as shown above. In such an instance, each repeating unit of a polymer according to Formula (A) should make up at least about 10 percent of all of the repeating units present in the polymer according to Formula (A). With regard to such polymers according to Formula (B), each repeating unit of a polymer according to Formula (B) should make up at least about 20 percent of all of the repeating units present in the polymer according to Formula (B). In all instances, the total of all dissimilar repeating units in such polymers adds up to 100 percent.

Co-Poly(ester urethane)s

In one embodiment, the present invention relates to co-poly(ester urethane)s according to Formula (C) made from the combination of at least two different di-p-toluenesulfonic acid salts of bis-(α -amino acid) α,ω -alkylene diester according to Formulas (Ia) and (Ib) and at least one active bis-carbonate diester of a diol according to Formula (III). The above compounds are reacted using a suitable polymerization reaction (e.g., a polycondensation reaction) to yield co-poly(ester urethane) polymers according to Formula (C) below:

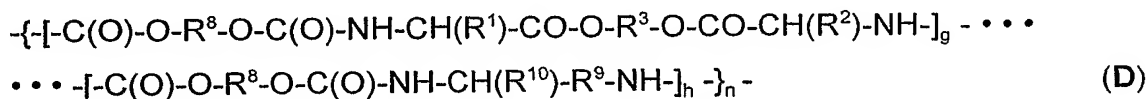


where R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^8 are as defined above; n is from about 10 to about 1000 and the ratio of e/f is in the range of about 90:10 to about 10:90. In another embodiment, the ratio of e/f is from about 75:25 to about 25:75; or even from about 60:40 to about 40:60. In another embodiment, n is from about 20 to about 500, or even from about 30 to about 300.

In one embodiment, the polymers according to Formula (C) have a Mw of about 5,000 to about 400,000 daltons. In another embodiment, the polymers according to Formula (C) have a Mw of about 10,000 to about 200,000 daltons, even about 20,000 to about 100,000 daltons.

5 In another embodiment, when two active bis-carbonate diesters of diols according to Formula (III) are reacted with two different di-p-toluenesulfonic acid salts of bis-(α -amino acid) α,ω -alkylene diester according to Formulas (Ia) and (Ib) the polymers produced thereby have a formula according to Formula (C) above except that the first R^8 group and the second R^8 group are different from one another.

10 In still another embodiment, the present invention relates to co-poly(ester urethane)s according to Formula (D) made from the combination of at least one di-p-toluenesulfonic acid salt of a bis-(α -amino acid) α,ω -alkylene diester according to Formula (Ia) and/or (Ib), at least one di-p-toluenesulfonic acid salt of an ester according to Formula (IV) and at least one active bis-carbonate diester of a diol according to Formula (III). In the discussion below Formula (Ia) is used. However, Formula (Ib) can be substituted for Formula (Ia) by changing the appropriate R groups in Formula (D) to match those contained in Formula (Ib). The above compounds are reacted using a suitable polymerization reaction (e.g., a polycondensation reaction) to yield co-poly(ester urethane) polymers according to Formula (D) below:



25 where R^1 , R^2 , R^3 , R^8 , R^9 and R^{10} are as defined above; n is from about 10 to about 1000 and the ratio of g/h is in the range of about 80:20 to about 20:80. In another embodiment, the ratio of g/h is from about 70:30 to about 30:70; or even from about 60:40 to about 40:60. In another embodiment, n is from about 20 to about 500, or even from about 30 to about 300.

In one embodiment, the polymers according to Formula (D) have a Mw of about 5,000 to about 400,000 daltons. In another embodiment, the polymers according to Formula (D) have a Mw of about 10,000 to about 200,000 daltons, even about 20,000 to about 100,000 daltons.

5 In another embodiment, when two active bis-carbonate diesters of diols according to Formula (III) are reacted with a di-p-toluenesulfonic acid salt of a bis-(α -amino acid) α,ω -alkylene diester according to Formula (Ia) or (Ib) and a di-p-toluenesulfonic acid salt of an ester according to Formula (IV) the polymers produced thereby have a formula according to Formula (D) above except that the
10 first R^8 group and the second R^8 group are different from one another. This situation occurs when one active bis-carbonate diester of a diol according to Formula (III) is pre-reacted with a di-p-toluenesulfonic acid salt of a bis-(α -amino acid) α,ω -alkylene diester according to Formula (Ia) or (Ib) and then the second active bis-carbonate diester of a diol according to Formula (III) and the a di-p-toluenesulfonic acid salt of
15 an ester according to Formula (IV) are added to the product of the pre-reaction and the combination is further reacted. In another embodiment, if all four compounds are combined together and reacted simultaneously, this combination can yield a copoly(ester urethane) having four different repeating units.

In yet still another embodiment, the copolymers according to Formulas (A)
20 and (B) contain three or more different repeating units rather than just two as shown above. In such an instance, each repeating unit of a polymer according to Formula (A) should make up at least about 10 percent of all of the repeating units present in the polymer according to Formula (A). With regard to such polymers according to Formula (B), each repeating unit of a polymer according to Formula (B) should make
25 up at least about 20 percent of all of the repeating units present in the polymer according to Formula (B). In all instances, the total of all dissimilar repeating units in such polymers adds up to 100 percent.

In yet still another embodiment, the copolymers according to Formulas (C)
30 and (D) contain three or more different repeating units rather than just two as shown above. In such an instance, each repeating unit of a polymer according to Formula (C) should make up at least about 10 percent of all of the repeating units present in

the polymer according to Formula (C). With regard to such polymers according to Formula (D), each repeating unit of a polymer according to Formula (D) should make up at least about 20 percent of all of the repeating units present in the polymer according to Formula (D). In all instances, the total of all dissimilar repeating units in such polymers adds up to 100 percent.

Polymerization Process:

The amounts and/or ratio of the reactants necessary to produce each of the above polymers according to Formulas (A) to (D) will be discussed in detail below after the completion of the discussion of the methods used to polymerize the chosen reactants.

In one embodiment, the polymers of the present invention are produced using a polycondensation reaction. In the polycondensation reaction of this embodiment, suitable amounts of the chosen starting materials are added to a suitable solvent (*e.g.*, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), methyl pyrrolidone (MP), hexamethyl phosphotriamide (HMPT), dimethyl sulfoxide (DMSO), N-methylcaprolactame, alcohols (such as trifluoroethanol), etc.). To this mixture is added a suitable amount of a tertiary amine initiator (*e.g.*, triethylamine (Et₃N), or a tertiary fatty amine (*e.g.*, N-methyl-morpholine, N,N'-dimethylpyperazine, N-methylpyperidine, sodium or potassium carbonates and/or hydrocarbonates, etc.)). The chosen reaction mixture is then mixed at a temperature of about 10 °C to about 40 °C in order to begin the polycondensation polymerization reaction. In another embodiment, the reaction components are mixed at a temperature of about 15 °C to about 35 °C, or even at a temperature of about 20 °C to about 30 °C.

After the chosen reaction components are thoroughly mixed the temperature of the reaction mixture is raised and held there for a suitable amount of time so as to complete the polycondensation polymerization reaction. In one embodiment, the reaction is conducted at a temperature in the range of about 60 °C to about 120 °C, or in the range of about 80 °C to about 100 °C, or even in the range of about 85 °C to about 95 °C. The reaction is carried out for about 8 to about 16 hours, or for about 10 to about 14 hours, or even for about 11 to about 13 hours.

After the above reaction is complete, the reaction product is allowed to cool to room temperature, and the product is cast as a thin film onto any suitably smooth surface (*e.g.*, a metal or plastic plate), and washed with water (distilled, de-ionized, etc.). The polymer film obtained thereby is dried at a temperature in the range of about 20 °C to about 50 °C, or from about 25 °C to about 45 °C, or even from about 30 °C to about 40 °C, under a reduced pressure (*e.g.*, a pressure in the range of about 0.1×10^{-3} atms. to about 10×10^{-3} atms., or even a pressure in the range of about 0.5×10^{-3} atms. to about 8×10^{-3} atms., or even in the range of about 1×10^{-3} atms. to about 5×10^{-3} atms.). After drying, the polymer is purified using an extraction technique with any suitable organic solvent (*e.g.*, ethylacetate, butylacetate, diethyl ether, acetone, benzene, toluene, etc.) in a Soxhlett apparatus until a negative test for p-toluenesulfonic acid and p-nitrophenol is obtained (see the testing and purification procedures below).

With regard to the amounts and/or ratio of the reactants necessary to produce each of the above polymers according to Formulas (A) to (D), in the case of polymers according to Formula (A), the molar ratio of the total molar amount of Formulas (Ia) and (Ib) to the molar amount of Formula (II) needs to be approximately 1:1. This is necessary to produce high molecular weight polymers via the above described polycondensation reaction. In another embodiment, when low molecular weight polymers are desired, the molar ratio of the total molar amount of Formulas (Ia) and (Ib) to the molar amount of Formula (II) is in the range of about 5:1 to about 1:5. In another embodiment, the molar ratio of the total molar amount of Formulas (Ia) and (Ib) to the molar amount of Formula (II) is about 2.5:1 to about 1:2.5.

Furthermore, in the polymers according to Formula (A) the molar ratio of Formula (Ia) to Formula (Ib) is in the range of about 9:1 to about 1:9. In another embodiment, the molar ratio of Formula (Ia) to Formula (Ib) is about 7.5:2.5 to about 2.5:7.5; or even about 6:4 to about 4:6. In yet another embodiment, the molar ratio of Formula (Ia) to Formula (Ib) is about 1:1. The molar amount of Formula (II) present in the reaction mixture is at least equal to the total molar amount of Formulas (Ia) and (Ib).

In the case of polymers according to Formula (B), the molar ratio of the total molar amount of Formula (Ia) and/or (Ib) (if both are present) to the molar amount of Formula (IV) is in the range of about 8:2 to about 2:8. In another embodiment, the molar ratio of the total molar amount of Formula (Ia) and/or (Ib) to the molar amount of Formula (IV) is about 7:3 to about 3:7; or even about 6:4 to about 4:6. In yet another embodiment, the molar ratio of the total molar amount of Formula (Ia) and/or (Ib) to the molar amount of Formula (IV) is about 1:1.

The molar amount of Formula (II) present in the reaction mixture to produce polymers according to Formula (B) again depends on whether or not high molecular weight polymers are desired. If so, then the ratio of the total molar amount of Formula (Ia) and/or (Ib) and Formula (IV) to the molar amount of Formula (II) needs to be approximately 1:1. This is necessary to produce high molecular weight polymers via the above described polycondensation reaction. In another embodiment, when low molecular weight polymers are desired, the ratio of the total molar amount of Formula (Ia) and/or (Ib) and Formula (IV) to the molar amount of Formula (II) is in the range of about 5:1 to about 1:5. In another embodiment, the molar ratio of the total molar amount of Formula (Ia) and/or (Ib) and Formula (IV) to the molar amount of Formula (II) is about 2.5:1 to about 1:2.5.

In the case of polymers according to Formula (C), the molar ratio of Formula (Ia) to Formula (Ib) is in the range of about 9:1 to about 1:9. In another embodiment, the molar ratio of Formula (Ia) to Formula (Ib) is about 7.5:2.5 to about 2.5:7.5; or even about 6:4 to about 4:6. In yet another embodiment, the molar ratio of Formula (Ia) to Formula (Ib) is about 1:1.

The molar amount of Formula (III) present in the reaction mixture to produce polymers according to Formula (C) again depends on whether or not high molecular weight polymers are desired. If so, then the ratio of the total molar amount of Formulas (Ia) and (Ib) to the molar amount of Formula (III) needs to be approximately 1:1. This is necessary to produce high molecular weight polymers via the above described polycondensation reaction. In another embodiment, when low molecular weight polymers are desired, the ratio of the total molar amount of Formulas (Ia) and (Ib) to the molar amount of Formula (III) is in the range of about

5:1 to about 1:5. In another embodiment, the molar ratio of the total molar amount of Formulas (Ia) and (Ib) to the molar amount of Formula (III) is about 2.5:1 to about 1:2.5.

5 In the case of polymers according to Formula (D), the molar ratio of the total molar amount of Formula (Ia) and/or (Ib) (if both are present) to the molar amount of Formula (IV) is in the range of about 8:2 to about 2:8. In another embodiment, the molar ratio of the total molar amount of Formula (Ia) and/or (Ib) to the molar amount of Formula (IV) is about 7:3 to about 3:7; or even about 6:4 to about 4:6. In yet another embodiment, the molar ratio of the total molar amount of Formula (Ia) and/or (Ib) to the molar amount of Formula (IV) is about 1:1.

10 The molar amount of Formula (III) present in the reaction mixture to produce polymers according to Formula (D) again depends on whether or not high molecular weight polymers are desired. If so, then the ratio of the total molar amount of Formula (Ia) and/or (Ib) and Formula (IV) to the molar amount of Formula (III) needs to be approximately 1:1. This is necessary to produce high molecular weight polymers via the above described polycondensation reaction. In another embodiment, when low molecular weight polymers are desired, the ratio of the total molar amount of Formula (Ia) and/or (Ib) and Formula (IV) to the molar amount of Formula (III) is in the range of about 5:1 to about 1:5. In another embodiment, the molar ratio of the total molar amount of Formula (Ia) and/or (Ib) and Formula (IV) to the molar amount of Formula (III) is about 2.5:1 to about 1:2.5.

20 Furthermore, upon addition of the initiator to any of the reaction mixtures, the concentration of the combination of the solvent and the tertiary amine (e.g., DMF and Et₃N) is in the range of about 0.6 moles/L to about 1.8 moles/L in view of the amount of any one of Formulas (Ia), (Ib), (II), (III) and/or (IV) which is/are present in the reaction mixture. In another embodiment, the concentration of the combination of the solvent and the tertiary amine is in the range of about 0.8 moles/L to about 1.6 moles/L in view of the molar amount of any one of Formulas (Ia), (Ib), (II), (III) and/or (IV) which is/are present in the reaction mixture. In yet another embodiment, the

concentration of the solvent and the tertiary amine is in the range of about 0.9 moles/L to about 1.3 moles/L in view of the amount of any one of Formulas (Ia), (Ib), (II), (III) and/or (IV) which is/are present in the reaction mixture.

In yet another embodiment, when the reactants of the polymerization reaction are a combination of two di-p-toluenesulfonic acid salts of bis-(α -amino acid) α,ω -alkylene diester according to Formulas (Ia) and (Ib) (where (Ia) and (Ib) can be the same compound or different compounds) and with two active diesters according to Formula (II) or two active bis-carbonates according to Formula (III), the polycondensation polymerization reaction is carried out in a two step process.

In the first step, one of the above di-p-toluenesulfonic acid salt compounds according to Formula (Ia) or (Ib) is combined with one of the active diesters according to Formula (III) in a solvent. A suitable amount of a tertiary amine initiator is then added to this mixture. The reaction components are mixed at a temperature of about 10 °C to about 40 °C, or at a temperature of about 15 °C to about 35 °C, or even at a temperature of about 20 °C to about 30 °C. The reaction is carried out for about 2 to about 6 hours, or for about 3 to about 5 hours, or even for about 4 hours, in order to begin a portion of the overall polycondensation reaction.

After this first step is complete, the remaining di-p-toluenesulfonic acid salt compound according to Formula (Ia) or (Ib) and the remaining active diester according to Formula (II) are added to the above reaction mixture. The combined reaction mixture is mixed and the temperature of the reaction mixture is raised and held there for a suitable amount of time so as to complete the polycondensation polymerization reaction. In one embodiment, the reaction is conducted at a temperature in the range of about 60 °C to about 120 °C, or in the range of about 80 °C to about 100 °C, or even in the range of about 85 °C to about 95 °C. This reaction is carried out for about 8 to about 16 hours, or for about 10 to about 14 hours, or even for about 11 to about 13 hours.

The above reaction produces a polymer with only two types of repeating units because the first step ensures almost complete reaction of the first di-p-toluenesulfonic acid salt compound according to Formula (Ia) or (Ib) with one of the active diesters according to Formula (III). The second step accomplishes the

reaction of the second di-p-toluenesulfonic acid salt compound according to Formula (Ia) or (Ib) with the second active diesters according to Formula (III) and the linking of the first and second repeating units to form a polymer according to Formula (A). This same process can also be used to form polymers according to Formula (C) when two bis-carbonates according to Formula (III) are used instead of two active diesters according to Formula (II).

The product of these reactions are then subjected to similar processing steps as discussed above.

Purification Process for Co-Poly(ester amide)s (Co-PEAs):

The following process is used to purify the Co-PEAs according to the present invention. The co-poly(ester amide) polymer obtained according to the present invention is dissolved in a sufficient amount of chloroform (usually about 50 to about 100 ml of solvent per about 10 grams of polymer). This solution is filtered and the polymer is precipitated in butyl acetate (about 1.0 L), upon which the polymer separates as a tar like mass, and is then kept overnight in a refrigerator. The next morning, the butyl acetate is removed and a fresh portion of butyl acetate (again about 1.0 L) is added to the tar like mass and it is again kept overnight in a refrigerator again. This procedure is repeated until a negative test for p-nitrophenol and p-toluenesulfonic acid (see below) is obtained. In one embodiment, it is repeated 2 to 10 times, in another 2 to 8 times, in another 2 to 4 times. However, it should be realized that it can take more repetitions than stated above to purify the polymer(s) obtained using the present inventive methods. After such treatment is complete, p-nitrophenol and p-toluenesulfonic acid (which are more soluble in butyl acetate than in water) are nearly completely removed from the polymer.

Next, the tar like mass there obtained is dried, dissolved in chloroform, cast onto hydrophobic surface, chloroform evaporated to dryness, and dried at about 60 °C under reduced pressure (e.g., a pressure in the range of about 0.1×10^{-3} atms. to about 10×10^{-3} atms., or even a pressure in the range of about 0.5×10^{-3} atms. to about 8×10^{-3} atms., or even in the range of about 1×10^{-3} atms. to about 5×10^{-3} atms.).

Purification Process for Co-Poly(ester urethane)s (Co-PEURs):

The following process is used to purify the Co-PEURs according to the present invention. The polymer obtained according to the present invention is dissolved in a sufficient amount of chloroform (usually about 50 to about 100 ml of solvent per about 10 grams of polymer) cast as a thin film onto a cylindrical glass vessel's (d = 400 - 500 mm) inner surface, dried at room temperature, washed with water, and dried again. The film obtained is dissolved in a suitable solvent (*e.g.*, DMF), and then the polymer is precipitated in water. A rubber-like polymer is collected and is dried at about 35 °C to about 40 °C under reduced pressure (*e.g.*, a pressure in the range of about 0.1×10^{-3} atms. to about 10×10^{-3} atms., or even a pressure in the range of about 0.5×10^{-3} atms. to about 8×10^{-3} atms., or even in the range of about 1×10^{-3} atms. to about 5×10^{-3} atms.). This procedure is repeated several times, until a negative test for p-nitrophenol and p-toluenesulfonic acid is obtained (see below). In one embodiment, it is repeated 2 to 10 times, in another 2 to 8 times, in another 3 to 4 times.

However, it should be realized that it can take more repetitions than stated above to purify either type of polymer obtained using the present inventive methods. After such treatment is complete, p-nitrophenol and p-toluenesulfonic acid are nearly completely removed from the desired polymer.

Testing Procedure for p-Nitrophenol:

The polymers of the present invention can be tested for the presence of p-nitrophenol by a variety of methods. One such method involves taking an appropriate amount of polymer to be purified (in one case about 200 to about 250 mg) and dissolving the polymer in an adequate amount of a boiling 10% water solution of NaOH. The resulting solution is then analyzed using UV-VIS spectrophotometer (Specord UV-VIS, Carl Zeiss, Jena, cell of 4 ml, $\ell = 1.0$ cm). The samples are tested for the absence of absorption in the region of 430 nm ($\text{O}_2\text{NC}_6\text{H}_4\text{O}^-$) which indicates that no p-nitrophenol exists in the polymeric sample to any appreciable degree. It is noted that in alkaline media, p-nitrophenol does not absorb in UV region. As such, its absorption does not overlap the absorption of

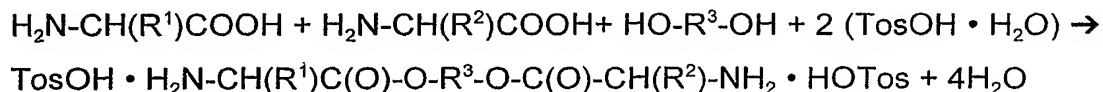
phenylalanine that comes from the polymers. The absence of absorption in the region of 240 to 250 nm ($p\text{-CH}_3\text{-C}_6\text{H}_4\text{-SO}_3^-$) indicates that no p-toluenesulfonic acid exists in the polymeric sample to any appreciable degree (this is true for those copolymers which are free of phenylalanine).

5 Testing Procedure for p-Toluenesulfonic Acid:

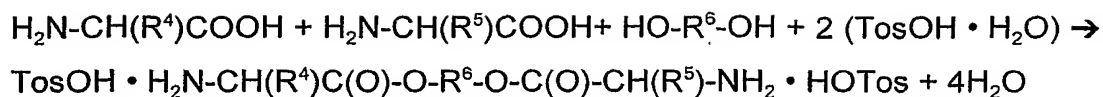
The testing procedure utilized herein for p-toluenesulfonic acid is identical to that used to test for p-nitrophenol (i.e., UV determination). The phenyl group present in TosOH absorbs in the region of 240 to 260 nm. However, since the benzyl groups of phenylalanine absorb in the same region, the testing procedure is
 10 utilized on co-poly(ester amide)s (PEAs) and co-poly(ester urethane)s (PEURs) free of phenylalanine. In all the cases studied, no absorbance of TosOH was observed when the absorbance of p-nitrophenol was not observed. This is the expected result since the solubility of TosOH in water is much higher than the solubility of p-nitrophenol and thus, in this instance, all or almost all of the TosOH is removed prior
 15 to the removal of the p-nitrophenol.

Synthesis of Di-p-toluenesulfonic Acid Salts of Bis-(α -amino acid) α,ω -alkylene Diesters:

Di-p-toluenesulfonic acid salts of bis-(α -amino acid) α,ω -alkylene diesters useful in the above-mentioned processes can be synthesized by a variety of
 20 methods. For example, one such method is shown below:



where R^1 , R^2 and R^3 are as defined above. This reaction yields the compounds represented by Formula (Ia). Alternatively, the following reaction is can
 25 be conducted:

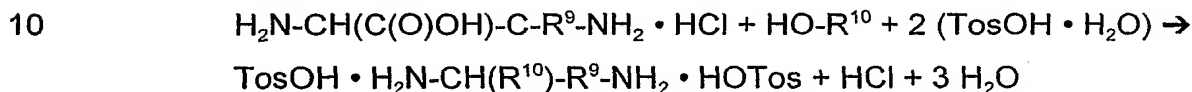


where R⁴, R⁵ and R⁶ are as defined above. This reaction yields the compounds represented by Formula (Ib).

5 Synthesis of Di-p-toluenesulfonic

Acid Salts of an Ester:

Di-p-toluenesulfonic acid salts of an ester useful in the above-mentioned processes can be synthesized by a variety of methods. For example, one such method for synthesizing such compounds is shown below:



where R⁹ and R¹⁰ are as defined above. This reaction yields the compounds represented by Formula (IV).

Synthesis of Active Diesters:

15 Active diesters for use in the present invention can be synthesized by a variety of methods. For example, one such method for synthesizing such diesters is shown below. The reaction is conducted in a suitable organic solvent.

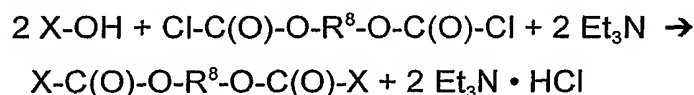


where R⁷ and X are as defined above; and Py is pyridine. This reaction yields the

20 compounds represented by Formula (II).

Synthesis of Active Bis-Carbonates of a Diol:

Active bis-carbonates for use in the present invention can be synthesized by a variety of methods. For example, one such method for synthesizing such bis-carbonates is shown below. The reaction is conducted in a suitable solvent (e.g., chlorobenzene).



where R^8 and X are as defined above; and Et_3N is defined above. This reaction yields the compounds represented by Formula (III).

Examples of Preparation of Polymers:

The Examples below are illustrative of the above-mentioned polymer reactions and are not to be construed as limiting. In the Examples below the reduced viscosity data (η_{red}) of the polymers is obtained in m-cresol at a concentration of 0.5 g/dL and a temperature of about 25 °C. Additionally, unless otherwise specified, the term a reduced pressure in the Examples below is equal to a pressure in the range of about 1×10^{-3} to about 5×10^{-3} atms.

Co-Poly(ester amide) (Co-PEA) Examples:Example 1:

Co-poly- $\{[\text{N,N'-adipoyl-[bis-(L-phenylalanine)-1,2-ethylene diester}]]_{0.80}\text{-}[\text{N,N'-adipoyl-[bis(L-leucine)-1,3-propylene diester}]]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture a di-p-toluenesulfonic acid salt of bis-(L-phenylalanine)-1,2-ethylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_2-$) (56.0672 g, 0.08 moles); di-p-toluenesulfonic acid salt of bis-(L-leucine)-1,3-propylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_3-$) (12.9766 g, 0.02 moles) (total

amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 96 %; the $\eta_{\text{red.}}$ = 0.76 dL/g; and the T_g is 52 °C (DSC). Additionally, the copolymer is soluble in chloroform, DMF, DMA, and DMSO; and insoluble in THF.

Example 2:

Co-poly- $\{[\text{N},\text{N}'\text{-sebacoyl-}[\text{bis-}(\text{L-phenylalanine})\text{-1,3-propylene diester}]]_{0.80}\text{-}[\text{N},\text{N}'\text{-sebacoyl-}[\text{bis-}(\text{L-leucine})\text{-1,4-butylene diester}]]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of bis(L-phenylalanine)-1,3-propylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_3-$) (57.1888 g, 0.08 moles); a di-p-toluenesulfonic acid salt of bis-(L-leucine)-1,4-butylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_4-$) (13.2170 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 98 %; the $\eta_{\text{red.}}$ = 1.06 dL/g; and the T_g is

45 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 46,000$ and the $M_n = 27,000$, and the $M_w/M_n = 1.7$ (GPC in THF).

Example 3:

5 Co-poly- $\{[N,N'$ -adipoyl-[bis-(L-phenylalanine)-1,4-butylene diester]] $_{0.80}$ -[N,N'-adipoyl-[bis-(L-valine)-1,4-butylene diester]] $_{0.20}\}$

10 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of bis-(L-phenylalanine)-1,4-butylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_4-$) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salt of bis(L-valine)-1,4-butylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_4-$) (12.6560 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

15 The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett
20 apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 97 %; the $\eta_{\text{red.}} = 0.76$ dL/g; and the T_g is 52 °C (DSC). Additionally, the copolymer is soluble in chloroform, DMF, DMA, and DMSO; and insoluble in THF.

Example 4:

25 Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] $_{0.80}$ -[N,N'-sebacoyl-[bis-(L-valine)-1,6-hexylene diester]] $_{0.20}\}$

30 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of di-p-toluenesulfonic acid salt of a bis(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (60.5552 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a bis-(L-valine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (13.2170 g, 0.02 moles)

(total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 %; the $\eta_{\text{red.}} = 1.24$ dL/g; and the T_g is 31.5 °C (DSC). Additionally, the copolymer is soluble in chloroform, DMF, DMA, and DMSO; and insoluble in THF.

Example 5:

Co-poly- $\{[\text{N},\text{N}'\text{-sebacoyl-}[\text{bis-}(\text{L-phenylalanine})\text{-1,6-hexylene diester}]]_{0.80}\text{-}[\text{N},\text{N}'\text{-sebacoyl-}[\text{bis-}(\text{L-isoleucine})\text{-1,4-butylene diester}]]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of di-p-toluenesulfonic acid salt of a bis(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (60.5552 g, 0.08 moles) and a di-p-toluenesulfonic acid salt of a bis-(L-isoleucine)-1,4-butylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ and R^6 is $-(\text{CH}_2)_4-$) (13.2170 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 %; the $\eta_{\text{red.}} = 0.98$ dL/g; and the T_g is

32 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 43,000$ and the $M_n = 28,500$, and the $M_w/M_n = 1.51$ (GPC in THF).

Example 6:

Co-poly- $\{[N,N'$ -adipoyl-(bis-(L-phenylalanine)-1,4-butylene diester)] $\}_{0.80}$ - $[N,N'$ -adipoyl-[bis(L-isoleucine)-1,6-hexylene diester)] $\}_{0.20}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,4-butylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_4-$) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a bis-(L-isoleucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ and R^6 is $-(\text{CH}_2)_6-$) (13.7782 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 98 %; the $\eta_{\text{red.}} = 1.16$ dL/g; and the T_g is 36 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 48,600$ and the $M_n = 29,800$, and the $M_w/M_n = 1.63$ (GPC in THF).

Example 7:

Co-poly- $\{[N,N'$ -adipoyl-[bis-(L-phenylalanine)-1,4-butylene diester)] $\}_{0.80}$ - $[N,N'$ -adipoyl-[bis-(DL-norleucine)-1,4-butylene diester)] $\}_{0.20}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,4-butylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_4-$) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a bis(DL-norleucine)-1,4-butylene diester (Formula

(Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and R^6 is $-(\text{CH}_2)_4-$ (13.2170 g, 0.02 moles) (total amount of the salts is 0.1 mole); and a di-p-nitrophenyl adipate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3ml) at room temperature.

5 The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett
10 apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 %; the $\eta_{\text{red.}} = 1.45 \text{ dL/g}$; and the T_g is 42 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 8:

15 Co-poly- $\{[\text{N},\text{N}'\text{-adipoyl-[bis-(L-phenylalanine)-1,4-butylene diester]}]_{0.80}\text{-}[\text{N},\text{N}'\text{-adipoyl-[bis-(L-leucine)-1,6-hexylene diester]}]_{0.20}\}$

 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,4-butylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_4-$) (58.3112 g, 0.08 moles); a
20 di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (13.7782 g, 0.02 moles) (total amount of the salts is 0.1 mole); and a di-p-nitrophenyl adipate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

25 The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett
30 apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 %; the $\eta_{\text{red.}} = 1.36 \text{ dL/g}$; and the T_g is

44 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 52,400$ and the $M_n = 33,500$, and the $M_w/M_n = 1.56$ (GPC in THF).

Example 9:

5 Co-poly- $\{[N,N'$ -adipoyl-[bis-(L-phenylalanine)-1,4-butylene diester]] $_{0.80}$ -[N,N'-adipoyl-[bis-(L-leucine)-1,8-octylene diester]] $_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,4-butylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_4-$) (58.3112 g, 0.08 moles); a
10 di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,8-octylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_8-$) (14.3392 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

15 The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett
20 apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 %; the $\eta_{\text{red.}} = 1.42$ dL/g; and the T_g is 32 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 10:

25 Co-poly- $\{[N,N'$ -adipoyl-[bis-(L-phenylalanine)-1,4-butylene diester]] $_{0.80}$ -[N,N'-adipoyl-[bis-(L-leucine)-1,12-dodecylene diester]] $_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,4-butylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_4-$) (58.3112 g, 0.08 moles); a
30 di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,12-dodecylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_{12}-$) (15.4614 g, 0.02

moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 96 %; the $\eta_{\text{red.}}$ = 0.58 dL/g; and the T_g is 26 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 11:

Co-poly- $\{[\text{N},\text{N}'\text{-adipoyl-}[\text{bis-}(\text{L-phenylalanine})\text{-1,4-butylene diester}]]_{0.80}\text{-}[\text{N},\text{N}'\text{-adipoyl-}[\text{bis-}(\text{DL-methionine})\text{-1,4-butylene diester}]]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,4-butylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_4-$) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a bis(DL-methionine)-1,4-butylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}_2\text{SCH}_3$ and R^6 is $-(\text{CH}_2)_4-$) (13.9386 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-

toluenesulfonic acid is received, the yield is 99 %; the $\eta_{\text{red.}} = 1.44$ dL/g; and the T_g is 22 °C (DSC). Additionally, the copolymer is soluble in chloroform, DMF, DMA, and DMSO.

Example 12:

Co-poly- $\{[N,N'$ -adipoyl-[bis-(L-phenylalanine)-1,4-butylene diester]] $\}_{0.80}$ - $[N,N'$ -adipoyl-[bis-(DL-methionine)-1,6-hexylene diester]] $\}_{0.20}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,4-butylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_4-$) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a bis(DL-methionine)-1,4-butylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}_2\text{SCH}_3$ and R^6 is $-(\text{CH}_2)_6-$) (14.4996 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 %; the $\eta_{\text{red.}} = 1.28$ dL/g; and the T_g is 18 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 47,800$ and the $M_n = 25,500$, and the $M_w/M_n = 1.87$ (GPC in THF).

Example 13:

Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] $\}_{0.90}$ - $[N,N'$ -sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] $\}_{0.10}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (68.1246 g, 0.09 moles); di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib),

where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$ (6.8891 g, 0.01 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

5 The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett
10 apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 %; the $\eta_{\text{red.}} = 1.54$ dL/g; and the T_g is 36 °C (DSC). Additionally, the copolymer is soluble in chloroform, DMF, DMA, and DMSO; and insoluble in THF.

Example 14:

15 Co-poly- $\{[\text{N},\text{N}'\text{-sebacoyl-}[\text{bis-}(\text{L-phenylalanine})\text{-1,6-hexylene diester}]]_{0.80}\text{-}[\text{N},\text{N}'\text{-sebacoyl-}[\text{bis-}(\text{L-leucine})\text{-1,6-hexylene diester}]]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (60.5552 g (0.08 moles); a
20 di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (13.7782 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

25 The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett
30 apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 %; the $\eta_{\text{red.}} = 1.48$

dL/g; and the T_g is 34 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 63,200$ and the $M_n = 38,800$, and the $M_w/M_n = 1.63$ (GPC in THF).

Example 15:

5 Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] $_{0.60}$ -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] $_{0.40}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (45.4146 g, 0.06 moles); a
10 di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (27.5564 g, 0.04 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

15 The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett
20 apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 %; the $\eta_{\text{red.}} = 1.44$ dL/g; and the T_g is 35 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 62,000$ and the $M_n = 33,400$, and the $M_w/M_n = 1.86$ (GPC in THF).

25 Example 16:

Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] $_{0.40}$ -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] $_{0.60}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (30.2776 g, 0.04 moles); a
30 di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib),

where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$ (41.3346 g, 0.06 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 %; the $\eta_{\text{red.}} = 1.32 \text{ dL/g}$; and the T_g is 34 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 60,000$ and the $M_n = 36,200$, and the $M_w/M_n = 1.66$ (GPC in THF).

Example 17:

Co-poly- $\{[\text{N,N}'\text{-sebacoyl-}[\text{bis-}(\text{L-phenylalanine})\text{-1,6-hexylene diester}]]_{0.20}\text{-}[\text{N,N}'\text{-sebacoyl-}[\text{bis-}(\text{L-leucine})\text{-1,6-hexylene diester}]]_{0.80}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (15.1388 g, 0.02 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (55.1128 g, 0.08 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-

toluenesulfonic acid is received, the yield is approximately 100 %; the $\eta_{\text{red.}}$ = 1.52 dL/g; and the T_g is 34 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The M_w = 65,300 and the M_n = 38,400, and the M_w/M_n = 1.70 (GPC in THF).

5 Example 18:

Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] $\}_{0.10}$ - $[N,N'$ -sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] $\}_{0.90}\}$

10 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (7.5694 g, 0.01 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (62.0019 g, 0.09 moles) (total amount of the salts is 0.1 mole); and a di-p-nitrophenyl sebacinate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF
15 (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The
20 resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 %; the $\eta_{\text{red.}}$ = 1.42 dL/g; and the T_g is 35 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The M_w = 58,800 and the M_n = 37,000, and the
25 M_w/M_n = 1.59 (GPC in THF).

Example 19:

Co-poly- $\{[N,N'$ -tetradecandioyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] $\}_{0.80}$ - $[N,N'$ -tetradecandioyl-[bis-(L-leucine)-1,6-hexylene diester]] $\}_{0.20}\}$

30 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (60.5552 g, 0.08 moles); a

di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (13.7782 g, 0.02 moles) (total amount of the salts is 0.1 mole); and a di-p-nitrophenyl tetradecandioate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_{12}-$) (50.055 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 %; the $\eta_{\text{red.}} = 1.27$ dL/g; and the T_g is 28 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 20:

Co-poly- $\{[\text{N},\text{N}'\text{-docosanedioyl-}[\text{bis-}(\text{L-phenylalanine})\text{-1,6-hexylene diester}]]_{0.80}\text{-}[\text{N},\text{N}'\text{-docosanedioyl-}[\text{bis-}(\text{L-leucine})\text{-1,6-hexylene diester}]]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salts of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (60.5552 g, 0.08 moles); a di-p-toluenesulfonic acid salts of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (13.7782 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl docosanedioate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_{20}-$) (61.277 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-

toluenesulfonic acid is received, the yield is approximately 100 %; and the $\eta_{\text{red.}}$ = 0.78 dL/g. Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 21:

5 Co-poly- $\{[N,N'$ -sebacoyl- $[\text{bis}-(L\text{-phenylalanine})\text{-}1,6\text{-hexylene diester}]]_{0.50}\text{-}[N,N'$ -adipoyl- $[\text{bis}-(L\text{-leucine})\text{-}1,6\text{-hexylene diester}]]_{0.50}\}$

Dry triethylamine (15.4 ml, 0.11 moles) is added to a mixture of a di-*p*-toluenesulfonic acid salt of a bis-(*L*-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (37.8470 g, 0.05 moles)
 10 and a di-*p*-nitrophenyl sebacinate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (22.2220 g, 0.05 moles) in dry DMF (52.5 ml) at room temperature and is stirred for about 4 hours. Next, a di-*p*-toluenesulfonic acid salt of a bis-(*L*-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (34.4455 g, 0.05 moles) (total amount of the salts is 0.1 moles); di-*p*-
 15 nitrophenyl adipate (Formula (II), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (19.4165 g, 0.05 moles; total amount of the diesters is 0.1 moles); and an additional 15.4 ml (0.11 moles) of Et_3N (total volume of DMF and Et_3N is 83.3 ml) is added to the reaction mixture and the temperature is increased to about 90 °C and is stirred for about 12 hours.

20 Next, the reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for *p*-nitrophenol and *p*-toluenesulfonic acid is received, the yield is 98 %; the $\eta_{\text{red.}}$ = 1.22 dL/g; and the T_g is
 25 36 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 22:

30 Co-poly- $\{[N,N'$ -adipoyl-bis-(*L*-phenylalanine)-1,6-hexylene diester] $_{0.50}\text{-}[N,N'$ -sebacoyl- $[\text{bis}-(L\text{-leucine})\text{-}1,6\text{-hexylene diester}]]_{0.50}\}$

Dry triethylamine (15.4 ml, 0.11 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R¹ and R² both are -CH₂Ph and R³ is -(CH₂)₆-) (37.8470 g, 0.05 moles) and a di-p-nitrophenyl adipate (Formula (II), where X is -O-C₆H₄-NO₂ and R⁷ is -(CH₂)₄-) (19.4165 g, 0.05 moles) in dry DMF (52.5 ml) at room temperature and is stirred for about 4 hours. Next, a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R⁴ and R⁵ both are -CH₂CH(CH₃)₂ and R⁶ is -(CH₂)₆-) (34.4455 g, 0.05 moles) (total amount of the salts is 0.1 moles); a di-p-nitrophenyl sebacinate (Formula (II), where X is -O-C₆H₄-NO₂ and R⁷ is -(CH₂)₈-) (22.2220 g, 0.05 moles), and an additional 15.4 ml (0.11 moles) of Et₃N (total volume of DMF and Et₃N is 83.3 ml) is added to the reaction mixture and the temperature is increased up to about 90 °C and is stirred for about 12 hours.

Next, the reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 98 %; the $\eta_{red.}$ = 1.22 dL/g; and the T_g is 35 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 23:

Co-poly- $\{[N,N'$ -adipoyl-bis-(L-phenylalanine)-1,2-ethylene diester] $\}_{0.80}$ - $[N^{\alpha},N^{\epsilon}$ -adipoyl-L-lysine n-octyl ester] $\}_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,2-ethylene diester (Formula (Ia), where R¹ and R² both are -CH₂Ph and R³ is -(CH₂)₂-) (56.0672 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R⁹ is -CH- and R¹⁰ is -C(O)-O-C₈H₁₇) (12.0563 g, 0.02 moles) (total amount of the salts is 0.1 moles); and di-p-nitrophenyl adipate (Formula (II) where X is -O-C₆H₄-NO₂ and R⁷ is -(CH₂)₄-) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et₃N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The viscous reaction solution is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. Next, the polymer is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 98 %; the $\eta_{\text{red.}}$ = 0.88 dL/g; and the T_g is 48 °C (DSC). Additionally, the copolymer is soluble in chloroform, DMF, DMA, and DMSO.

Example 24:

Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-phenylalanine)-1,3-propylene diester] $\}_{0.80}$ - $[N^\alpha,N^\epsilon$ -sebacoyl-L-lysine n-octyl ester] $\}_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,3-propylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_3-$) (57.1888 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (12.0563 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The viscous reaction solution is cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. Next, the polymer is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid, the yield is 98 %; the $\eta_{\text{red.}}$ = 1.06 dL/g; and the T_g is 45 °C (DSC). The copolymer is soluble in chloroform, THF, DMF, DMA, DMSO. The M_w = 46,000 and the M_n = 27,000, and the M_w/M_n = 1.7 (GPC in THF).

Example 25:

Co-poly- $\{[N,N'$ -adipoyl-bis-(L-phenylalanine)-1,4-butylene diester] $\}_{0.80}$ - $[N^{\alpha},N^{\epsilon}$ -adipoyl-L-lysine n-octyl ester] $\}_{0.20}\}$

5 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,4-butylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_4-$) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (12.0563 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 98 %; the $\eta_{\text{red.}} = 0.85$ dL/g; and the T_g is 46 °C (DSC). The copolymer is soluble in chloroform, DMF, DMA, and DMSO.

20 Example 26:

Co-poly- $\{[N,N'$ -adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] $\}_{0.90}$ - $[N^{\alpha},N^{\epsilon}$ -adipoyl-L-lysine n-octyl ester] $\}_{0.10}\}$

25 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (68.1246 g, 0.09 moles) and a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (6.0282 g, 0.01 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 97 %; the $\eta_{\text{red.}}$ = 1.12 dL/g; and the T_g is 40.5 °C (DSC). The copolymer is soluble in chloroform, DMF, DMA, and DMSO.

Example 27:

Co-poly- $\{[N,N'$ -adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] $_{0.80}$ - $[N^{\alpha},N^{\epsilon}$ -adipoyl-L-lysine n-octyl ester] $_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 $-(\text{CH}_2)_6-$) (60.5552 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}_2-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (12.0563 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 % and the $\eta_{\text{red.}}$ = 1.08 dL/g. The copolymer is soluble in chloroform, DMF, DMA, and DMSO.

Example 28:

Co-poly- $\{[N,N'$ -adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] $_{0.60}$ - $[N^{\alpha},N^{\epsilon}$ -adipoyl-L-lysine n-octyl ester] $_{0.40}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (45.4164 g, 0.06 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (24.1128 g, 0.04 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 95 % and the $\eta_{\text{red.}} = 0.98 \text{ dL/g}$. The copolymer is soluble in chloroform, DMF, DMA, and DMSO.

Example 29:

Co-poly- $\{[\text{N},\text{N}'\text{-adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester}]_{0.40}\text{-}[\text{N}^\alpha,\text{N}^\epsilon\text{-adipoyl-L-lysine n-octyl ester}]_{0.60}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (30.2776 g, 0.04 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (36.1692 g, 0.06 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The

resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 98 % and the $\eta_{\text{red.}} = 0.83$ dL/g. The copolymer is soluble in chloroform, DMF, DMA, and DMSO.

5 Example 30:

Co-poly- $\{[N,N'$ -adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] $_{0.20}$ - $[N^{\alpha},N^{\epsilon}$ -adipoyl-L-lysine n-octyl ester] $_{0.80}\}$

10 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (15.1388 g, 0.02 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}-$) (48.2256 g, 0.08 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl adipate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and
15 Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The
20 resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 % and the $\eta_{\text{red.}} = 0.72$ dL/g. The copolymer is soluble in chloroform, DMF, DMA, and DMSO.

Example 31:

25 Co-poly- $\{[N,N'$ -adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] $_{0.10}$ - $[N^{\alpha},N^{\epsilon}$ -adipoyl-L-lysine n-octyl ester] $_{0.90}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (7.5694 g, 0.01 moles); a
30 di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}-$) (54.2538 g, 0.09 moles) (total amount of the salts is

0.1 moles); and a di-p-nitrophenyl adipate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_4-$) (38.833 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 96 % and the $\eta_{\text{red.}} = 0.84$ dL/g. The copolymer is soluble in chloroform, DMF, DMA, and DMSO.

Example 32:

Co-poly- $\{[\text{N},\text{N}'\text{-sebacoyl-bis-(L-phenylalanine)-1,6-hexylene diester}]_{0.80}-[\text{N}^{\alpha},\text{N}^{\epsilon}\text{-sebacoyl-L-lysine n-octyl ester}]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (60.5552 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}_2-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (12.0563 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 %; the $\eta_{\text{red.}} = 1.24$ dL/g; and the T_g is 31.5 °C (DSC). The copolymer is soluble in chloroform, DMF, DMA, and DMSO.

Example 33:

Co-poly- $\{[N,N\text{-sebacoyl-bis-(L-phenylalanine)-1,6-hexylene diester}]_{0.80}\text{-}[N^{\alpha},N^{\epsilon}\text{-sebacoyl-L-lysine n-dodecyl ester}]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (60.5552 g, 0.08 moles); di-p-toluenesulfonic acid salt of a L-lysine n-dodecyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C(O)-O-C}_{12}\text{H}_{25}$) (13.1786 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O-C}_6\text{H}_4\text{-NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 %; the $\eta_{\text{red.}} = 0.98 \text{ dL/g}$; and the T_g is 32 °C (DSC). The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 43,000$ and the $M_n = 28,500$, and the $M_w/M_n = 1.51$ (GPC in THF).

Example 34:

Co-poly- $\{[N,N'\text{-sebacoyl-bis-(L-phenylalanine)-1,6-hexylene diester}]_{0.80}\text{-}[N^{\alpha},N^{\epsilon}\text{-sebacoyl-L-lysine n-hexadecyl ester}]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (60.5552 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-hexadecyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C(O)-O-C}_{16}\text{H}_{33}$) (14.3008 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O-C}_6\text{H}_4\text{-NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 % and the $\eta_{\text{red.}} = 0.85$ dL/g. The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 35:

Co-poly- $\{[N,N'$ -tetradecandioyl-bis-(L-phenylalanine)-1,6-hexylene diester] $\}_{0.80}$ - $[N^{\alpha},N^{\epsilon}$ - tetradecandioyl-L-lysine n-octyl ester] $\}_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (60.5552 g, 0.08 moles); di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (12.0563 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl tetradecandioate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_{12}-$) (50.055 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 %; the $\eta_{\text{red.}} = 1.27$ dL/g; and the T_g is 28 °C (DSC). The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 36:

Co-poly- $\{[N,N'$ -docosanedioyl-bis-(L-phenylalanine)-1,6-hexylene diester] $\}_{0.80}$ - $[N^{\alpha},N^{\epsilon}$ - docosanedioyl-L-lysine n-octyl ester] $\}_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (60.5552 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (12.0563 g, 0.02 moles) (total amount of the salts is 0.1 mole); and a di-p-nitrophenyl docosanedioate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_{20}-$) (61.277 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 % and the $\eta_{\text{red.}} = 0.78$ dL/g. The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 37:

Co-poly- $\{[\text{N},\text{N}'\text{-sebacoyl-bis-(L-leucine)-1,6-hexylene diester}]_{0.90}-[\text{N}^\alpha,\text{N}^\epsilon\text{-sebacoyl-L-lysine n-octyl ester}]_{0.10}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^3 is $-(\text{CH}_2)_6-$) (62.0019 g, 0.09 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (6.0282 g, 0.01 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The

resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 %; the $\eta_{red.}$ = 1.30 dL/g; and the T_g is 26 °C (DSC). The copolymer is soluble in chloroform, ethanol, THF, DMF, DMA, and DMSO.

Example 38:

Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-leucine)-1,6-hexylene diester] $_{0.80}$ - $[N^\alpha,N^\epsilon$ -sebacoyl-L-lysine n-octyl ester] $_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^3 is $-(\text{CH}_2)_6-$) (55.1128 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (12.0563 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 98 %; the $\eta_{red.}$ = 1.08 dL/g; and the T_g is 21.5 °C (DSC). The copolymer is soluble in chloroform, ethanol, THF, DMF, DMA, and DMSO. The M_w = 41,800; the M_n = 23,500; and the M_w/M_n = 1.78 (GPC in THF).

Example 39:

Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-leucine)-1,6-hexylene diester] $_{0.60}$ - $[N^\alpha,N^\epsilon$ -sebacoyl-L-lysine n-octyl ester] $_{0.40}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^3 is $-(\text{CH}_2)_6-$) (41.3346 g, 0.06 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (24.1128 g, 0.04 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 %; the $\eta_{\text{red.}} = 1.18$ dL/g; and the T_g is 19 °C (DSC). The copolymer is soluble in chloroform, ethanol, THF, DMF, DMA, and DMSO.

Example 40:

Co-poly- $\{[\text{N},\text{N}'\text{-sebacoyl-bis-(L-leucine)-1,6-hexylene diester}]_{0.40}-[\text{N}^\alpha,\text{N}^\epsilon\text{-sebacoyl-L-lysine n-octyl ester}]_{0.60}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^3 is $-(\text{CH}_2)_6-$) (27.5564 g, 0.04 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (36.1692 g, 0.06 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric

product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 %; the $\eta_{\text{red.}}$ = 1.24 dL/g; and the T_g is 16 °C (DSC). The copolymer is soluble in chloroform, ethanol, THF, DMF, DMA, and DMSO.

Example 41:

Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-leucine)-1,6-hexylene diester] $\}_{0.20}$ - $[N^\alpha,N^\epsilon$ -sebacoyl-L-lysine n-octyl ester] $\}_{0.80}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^3 is $-(\text{CH}_2)_6-$) (13.7782 g, 0.02 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (48.2256 g, 0.08 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 98 % and the $\eta_{\text{red.}}$ = 0.99 dL/g. The copolymer is soluble in chloroform, ethanol, THF, DMF, DMA, and DMSO.

Example 42:

Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-leucine)-1,6-hexylene diester] $\}_{0.10}$ - $[N^\alpha,N^\epsilon$ -sebacoyl-L-lysine n-octyl ester] $\}_{0.90}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^3 is $-(\text{CH}_2)_6-$) (8.8891 g (0.01 moles);

a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (54.2538 g, 0.09 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 % and the $\eta_{\text{red.}} = 0.84 \text{ dL/g}$. The copolymer is soluble in chloroform, ethanol, THF, DMF, DMA, and DMSO.

Example 43:

Co-poly- $\{[\text{N},\text{N}'\text{-sebacoyl-bis-(L-valine)-1,6-hexylene diester}]_{0.80}-[\text{N}^{\alpha},\text{N}^{\epsilon}\text{-sebacoyl-L-lysine n-octyl ester}]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-valine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}(\text{CH}_3)_2$ and R^3 is $-(\text{CH}_2)_6-$) (52.8680 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (12.0563 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room

temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 % and the $\eta_{\text{red.}} = 1.35$ dL/g. The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 44:

5 Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-isoleucine)-1,6-hexylene diester] $_{0.80}$ - $[N^{\alpha},N^{\epsilon}$ -sebacoyl-L-lysine n-octyl ester] $_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-isoleucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ and R^3 is $-(\text{CH}_2)_6-$) (55.1128 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) 10 where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (12.0563 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^7 is $-(\text{CH}_2)_8-$) (44.444 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

15 The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room 20 temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is approximately 100 % and the $\eta_{\text{red.}} = 2.25$ dL/g. The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 45:

25 Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-phenylalanine)-1,6-hexylene diester] $_{0.60}$ - $[N,N'$ -sebacoyl-bis-(L-leucine)-1,6-hexylene diester] $_{0.20}$ - $[N^{\alpha},N^{\epsilon}$ -sebacoyl-L-lysine n-octyl ester] $_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (45.4164 g, 0.06 moles); a 30 di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib) where R^4 and R^5 are both $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (13.7782 g, 0.02 moles);

a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is -CH- and R^{10} is -C(O)-O-C₈H₁₇) (12.0564 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is -O-C₆H₄-NO₂ and R^7 is -(CH₂)₈-) (44.444 g, 0.1 moles) in DMF (52.5 ml) (total volume of DMF and Et₃N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 99 %; the $\eta_{red.}$ = 1.12 dL/g; and the T_g is 19 °C (DSC). The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 46:

Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-phenylalanine)-1,6-hexylene diester]_{0.40}-[N,N'-sebacoyl-bis-(L-leucine)-1,6-hexylene diester]_{0.40}-[N^α,N^ε-sebacoyl-L-lysine n-octyl ester]_{0.20}}

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both -CH₂Ph and R^3 is -(CH₂)₆-) (30.2776 g, 0.04 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib) where R^4 and R^5 are both -CH₂CH(CH₃)₂ and R^6 -(CH₂)₆-) (27.5564 g, 0.04 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is -CH- and R^{10} is -C(O)-O-C₈H₁₇) (12.0564 g, 0.02 moles) (total amount of the salts is 0.1 moles); and a di-p-nitrophenyl sebacinate (Formula (II) where X is -O-C₆H₄-NO₂ and R^7 is -(CH₂)₈-) (44.444 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et₃N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 80 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The

resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 98 %; the $\eta_{\text{red.}} = 1.06 \text{ dL/g}$; and the T_g is 18 °C (DSC). The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

5 Co-Poly(ester urethane) (Co-PEUR) Examples:

Example 47:

Co-poly- $\{[\text{N,N'-dimethylenedioxydicarbonyl-[bis-(L-phenylalanine)-1,4-butylene diester]]}_{0.80}\text{-}[\text{N,N'-dimethylenedioxydicarbonyl-[bis-(L-leucine)-1,4-butylene diester]]}_{0.20}\}$

10 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,4-butylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_4-$) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,4-butylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_4-$) (13.2170 g, 0.02 moles)
15 (total amount of the salts is 0.1 mole); and an active bis-carbonate (Formula (III), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_2-$) (39.2210 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature,
20 cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 88 %; the $\eta_{\text{red.}} = 0.52 \text{ dL/g}$; and the T_g is
25 23 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 48:

Co-poly- $\{[\text{N,N'-trimethylenedioxydicarbonyl-[bis-(L-phenylalanine)-1,4-butylene diester]]}_{0.80}\text{-}[\text{N,N'-trimethylenedioxydicarbonyl-[bis-(L-leucine)-1,4-butylene diester]]}_{0.20}\}$

30

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,4-butylene diester (Formula (Ia), where R¹ and R² both are -CH₂Ph and R³ is -(CH₂)₄-) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,4-butylene diester (Formula (Ib), where R⁴ and R⁵ both are -CH₂CH(CH₃)₂ and R⁶ is -(CH₂)₄-) (13.2170 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III), where X is -O-C₆H₄-NO₂ and R⁸ is -(CH₂)₃-) (40.624 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et₃N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 86 %; the $\eta_{red.}$ = 0.68 dL/g; and the T_g is 21 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The Mw = 46,600 and the Mn = 27,400, and the Mw/Mn = 1.70 (GPC in THF).

Example 49:

Co-poly-{[N,N'-trimethylenedioxydicarbonyl-[bis-(L-phenylalanine)-1,6-hexylene diester]]_{0.90}-[N,N'-trimethylenedioxydicarbonyl-[bis-(L-leucine)-1,6-hexylene diester]]_{0.10}}

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R¹ and R² both are -CH₂Ph and R³ is -(CH₂)₆-) (68.1246 g, 0.09 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R⁴ and R⁵ both are -CH₂CH(CH₃)₂ and R⁶ is -(CH₂)₆-) (6.8891 g, 0.01 moles) (total amount of the salts is 0.1 mole); and an active bis-carbonate (Formula (III), where X is -O-C₆H₄-NO₂ and R⁸ is -(CH₂)₃-) (40.624 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et₃N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 92 %; the $\eta_{\text{red.}}$ = 0.66 dL/g; and the T_g is 25 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 50:

Co-poly- $\{[N,N'$ -trimethylenedioxydicarbonyl-bis-(L-phenylalanine)-1,6-hexylene diester] $\}_{0.80}$ - $[N,N'$ -trimethylenedioxydicarbonyl-[bis-(L-leucine)-1,6-hexylene diester] $\}_{0.20}$

Dry triethylamine (30.8 ml; 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salts of bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salts of bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (13.2170 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_3-$) (40.624 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 82 %; the $\eta_{\text{red.}}$ = 0.68 dL/g; and the T_g is 19 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The M_w = 47,300 and the M_n = 27,300, and the M_w/M_n = 1.73 (GPC in THF).

Example 51:

Co-poly- $\{[N,N'$ -trimethylenedioxydicarbonyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] $_{0.60}$ -[N,N'-trimethylenedioxydicarbonyl-[bis-(L-leucine)-1,6-hexylene diester]] $_{0.40}\}$

5 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R¹ and R² both are -CH₂Ph and R³ is -(CH₂)₆-) (45.4164 g, 0.06 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R⁴ and R⁵ both are -CH₂CH(CH₃)₂ and R⁶ is -(CH₂)₆-) (27.5564 g, 0.04 moles)
10 (total amount of the salts is 0.1 mole); and an active bis-carbonate (Formula (III), where X is -O-C₆H₄-NO₂ and R⁸ is -(CH₂)₃-) (40.624 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et₃N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature,
15 cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 91 %; the $\eta_{red.}$ = 0.48 dL/g; and the T_g is
20 15 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The Mw = 37,900 and the Mn = 22,300, and the Mw/Mn = 1.70 (GPC in THF).

Example 52:

Co-poly- $\{[N,N'$ -trimethylenedioxydicarbonyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] $_{0.40}$ -[N,N'-trimethylenedioxydicarbonyl-[bis-(L-leucine)-1,6-hexylene diester]] $_{0.60}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R¹ and R² both are -CH₂Ph and R³ is -(CH₂)₆-) (30.2776 g, 0.04 moles); a
30 di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R⁴ and R⁵ both are -CH₂CH(CH₃)₂ and R⁶ is -(CH₂)₆-) (41.3346 g, 0.06 moles)

(total amount of the salts is 0.1 moles), and an active bis-carbonate (Formula (III), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_3-$) (40.624 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 90 %; the $\eta_{\text{red.}} = 0.50$ dL/g; and the T_g is 14 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 38,400$ and the $M_n = 22,000$, and the $M_w/M_n = 1.75$ (GPC in THF).

Example 53:

Co-poly- $\{[\text{N},\text{N}'\text{-trimethylenedioxydicarbonyl-}[\text{bis-(L-phenylalanine)-1,6-hexylene diester}]]_{0.20}\text{-}[\text{N},\text{N}'\text{-trimethylenedioxydicarbonyl-bis-(L-leucine)-1,6-hexylene diester}]]_{0.80}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (15.1388 g, 0.02 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (55.1128 g, 0.08 moles) (total amount of the salts is 0.1 mole); and an active bis-carbonate (Formula (III), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_3-$) (40.624 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-

toluenesulfonic acid is received, the yield is 86 %; the $\eta_{\text{red.}} = 0.54$ dL/g; and the T_g is 13 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 54:

5 Co-poly- $\{[N,N'$ -trimethylenedioxydicarbonyl-[bis-(L-phenylalanine)-1,6-hexylene diester] $\}_{0.10}$ - $[N,N'$ -trimethylenedioxydicarbonyl-[bis-(L-leucine)-1,6-hexylene diester] $\}_{0.90}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (7.5694 g, 0.01 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (62.0019 g, 0.09 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_3-$) (40.624 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 88 %; the $\eta_{\text{red.}} = 0.49$ dL/g; and the T_g is 11 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

25 Example 55:

Co-poly- $\{[N,N'$ -trimethylenedioxydicarbonyl-[bis-(L-phenylalanine)-1,6-hexylene diester] $\}_{0.80}$ - $[N,N'$ -trimethylenedioxydicarbonyl-[bis-(L-isoleucine)-1,6-hexylene diester] $\}_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (58.3112 g, 0.08 moles); a

di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ and R^6 is $-(\text{CH}_2)_6-$) (13.2170 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_3-$) (40.624 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 93 %; the $\eta_{\text{red.}} = 0.52 \text{ dL/g}$; and the T_g is 16 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 56:

Co-poly- $\{[\text{N,N}'\text{-trimethylenedioxydicarbonyl-}[\text{bis-(L-phenylalanine)-1,6-hexylene diester}]]_{0.80}\text{-}[\text{N,N}'\text{-trimethylenedioxydicarbonyl-}[\text{bis-(DL-methionine)-1,6-hexylene diester}]]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a bis-(DL-methionine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}_2\text{SCH}_3$ and R^6 is $-(\text{CH}_2)_6-$) (14.4996 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_3-$) (40.624 g, 0.1 moles) in dry DMF (52.5 ml ;total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett

apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 85 %; the $\eta_{\text{red.}} = 0.38$ dL/g; and the T_g is 9 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

5 Example 57:

Co-poly- $\{[N,N'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-}[\text{bis}-(\text{L-phenylalanine})\text{-}1,6\text{-hexylene diester}]]_{0.80}\text{-}[N,N'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-}[\text{bis}-(\text{L-leucine})\text{-}1,6\text{-hexylene diester}]]_{0.20}\}$

10 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (13.2170 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III),
15 where X is $-\text{O-C}_6\text{H}_4\text{-NO}_2$ and R^8 is $-(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_2-$) (43.633 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric
20 product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 88 %; the $\eta_{\text{red.}} = 0.65$ dL/g; and the T_g is 11 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA,
25 and DMSO. The $M_w = 45,000$ and the $M_n = 24,300$, and the $M_w/M_n = 1.85$ (GPC in THF).

Example 58:

30 Co-poly- $\{[N,N'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-}[\text{bis}-(\text{L-phenylalanine})\text{-}1,6\text{-hexylene diester}]]_{0.60}\text{-}[N,N'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-}[\text{bis}-(\text{L-leucine})\text{-}1,6\text{-hexylene diester}]]_{0.40}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (45.4164 g, 0.06 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (27.5564 g, 0.04 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$) (43.633 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 84 %; the $\eta_{\text{red.}} = 0.46 \text{ dL/g}$; and the T_g is 10.5 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 37,600$ and the $M_n = 23,300$, and the $M_w/M_n = 1.61$ (GPC in THF).

Example 59:

Co-poly- $\{[\text{N},\text{N}'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-}[\text{bis}-(\text{L-phenylalanine})\text{-}1,6\text{-hexylene diester}]]_{0.40}\text{-}[\text{N},\text{N}'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-}[\text{bis}-(\text{L-leucine})\text{-}1,6\text{-hexylene diester}]]_{0.60}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (30.2776 g, 0.04 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (41.3346 g, 0.06 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$) (43.633 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 89 %; the $\eta_{\text{red.}} = 0.54$ dL/g; and the T_g is 10 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 38,200$ and the $M_n = 22,800$, and the $M_w/M_n = 1.68$ (GPC in THF).

Example 60:

Co-poly- $\{[N,N'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-}[\text{bis}-(L\text{-phenylalanine})\text{-}1,6\text{-hexylene diester}]]_{0.20}\text{-}[N,N'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-}[\text{bis}-(L\text{-leucine})\text{-}1,6\text{-hexylene diester}]]_{0.80}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (15.1388 g, 0.02 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (55.1128 g, 0.08 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$) (43.633 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 85 %; the $\eta_{\text{red.}} = 0.62$ dL/g; and the T_g is

9 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 40,000$ and the $M_n = 23,200$, and the $M_w/M_n = 1.72$ (GPC in THF).

Example 61:

Co-poly- $\{[N,N'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-}[\text{bis}-(\text{L-phenylalanine})\text{-}1,6\text{-hexylene diester}]]_{0.10}\text{-}[N,N'-(3\text{-oxapentylene-1,6-dioxydicarbonyl})\text{-}[\text{bis}-(\text{L-leucine})\text{-}1,6\text{-hexylene diester}]]_{0.90}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia), where R^1 and R^2 both are $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (7.5694 g, 0.01 moles); a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ib), where R^4 and R^5 both are $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^6 is $-(\text{CH}_2)_6-$) (62.0019 g, 0.09 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III), where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$) (43.633 g, 0.1 moles) in dry DMF (52.5 ml; total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate in a Soxhlett apparatus. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 90 %; the $\eta_{\text{red.}} = 0.47 \text{ dL/g}$; and the T_g is 7 °C (DSC). Additionally, the copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 38,000$ and the $M_n = 22,600$, and the $M_w/M_n = 1.68$ (GPC in THF).

Example 62:

Co-poly- $\{[N,N'\text{-trimethylenedioxydicarbonyl-bis}-(\text{L-phenylalanine})\text{-}1,6\text{-hexylene diester}]_{0.80}\text{-}[N^\alpha,N^\beta\text{-trimethylenedioxydicarbonyl-L-lysine n-octyl ester}]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{Ph}$ and R^3 is $-(\text{CH}_2)_6-$) (58.3112 g, 0.08 moles); a

di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R⁹ is -CH- and R¹⁰ is -C(O)-O-C₈H₁₇) (12.0564 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III) where X is -O-C₆H₄-NO₂ and R⁸ is -(CH₂)₃-) (40.624 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et₃N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 88 %; the $\eta_{red.}$ = 0.68 dL/g; and the T_g is 13 °C (DSC). The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The Mw = 56,200; the Mn = 30,900; and the Mw/Mn = 1.82 (GPC in THF).

Example 63:

Co-poly-{[N,N'-trimethylenedioxydicarbonyl-bis-(L-leucine)-1,6-hexylene diester]_{0.80}-[N^α,N^ε-trimethylenedioxydicarbonyl-L-lysine n-octyl ester]_{0.20}}

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R¹ and R² are both -CH₂CH(CH₃)₂ and R³ is -(CH₂)₆-) (55.1128 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R⁹ is -CH- and R¹⁰ is -C(O)-O-C₈H₁₇) (12.0564 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III) where X is -O-C₆H₄-NO₂ and R⁸ is -(CH₂)₃-) (40.624 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et₃N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-

toluenesulfonic acid is received, the yield is 86 % the $\eta_{\text{red.}} = 0.72$ dL/g; and the T_g is 12 °C (DSC). The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 62,400$; the $M_n = 37,100$; and the $M_w/M_n = 1.68$ (GPC in THF).

Example 64:

5 Co-poly- $\{[N,N'$ -trimethylenedioxydicarbonyl-bis-(L-leucine)-1,6-hexylene diester] $_{0.80}$ - $[N^{\alpha},N^{\epsilon}$ - trimethylenedioxydicarbonyl-L-lysine n-dodecyl ester] $_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^3 is $-(\text{CH}_2)_6-$) (55.1128 g, 0.08 moles);
 10 a di-p-toluenesulfonic acid salt of a L-lysine n-dodecyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_{12}\text{H}_{25}$) (13.1786 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_3-$) (40.624 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et_3N is 83.3 ml) at room temperature.

15 The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room
 20 temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 90 %; and $\eta_{\text{red.}} = 0.62$ dL/g. The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 65:

25 Co-poly- $\{[N,N'$ -trimethylenedioxydicarbonyl-bis-(L-leucine)-1,6-hexylene diester] $_{0.80}$ - $[N^{\alpha},N^{\epsilon}$ -trimethylenedioxydicarbonyl-L-lysine n-hexadecyl ester] $_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^3 is $-(\text{CH}_2)_6-$) (55.1128 g, 0.08 moles);
 30 a di-p-toluenesulfonic acid salt of a L-lysine n-hexadecyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_{16}\text{H}_{33}$) (14.3008 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III) where X is

-O-C₆H₄-NO₂ and R⁸ is -(CH₂)₃- (40.624 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et₃N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 92 % and the $\eta_{red.}$ = 0.48 dL/g. The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 66:

Co-poly-{[N,N'-(3-oxapentylene-1,5-dioxydicarbonyl)-bis-(L-phenylalanine)-1,6-hexylene diester]_{0.80}-[N^α,N^ε-(3-oxapentylene-1,5-dioxydicarbonyl)-L-lysine n-octyl ester]_{0.20}}

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-phenylalanine)-1,6-hexylene diester (Formula (Ia) where R¹ and R² are both -CH₂Ph and R³ is -(CH₂)₆-) (58.3112 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R⁹ is -CH- and R¹⁰ is -C(O)-O-C₈H₁₇) (12.0564 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III) where X is -O-C₆H₄-NO₂ and R⁸ is -(CH₂)₂-O-(CH₂)₂-) (43.633 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et₃N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 89 %; the $\eta_{red.}$ = 0.62 dL/g; and the T_g is 12.6 °C (DSC). The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The Mw = 58,700; the Mn = 32,800; and the Mw/Mn = 1.79 (GPC in THF).

Example 67:

Co-poly- $\{[N,N'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-bis-(L-leucine)-1,6-hexylene diester}]_{0.80}\text{-}[N^{\alpha},N^{\epsilon}\text{-(3-oxapentylene-1,5-dioxydicarbonyl)-L-lysine n-octyl ester}]_{0.20}\}$

5 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^3 is $-(\text{CH}_2)_6-$ (55.1128 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-octyl ester (Formula (IV) where R^9 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_8\text{H}_{17}$) (12.0564 g, 0.02 moles) (total amount of the salts is
10 0.1 moles); and an active bis-carbonate (Formula (III) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and R^8 is $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$) (43.633 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature,
15 cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 91 %; the $\eta_{\text{red.}} = 0.57$ dL/g; and the T_g
20 10.6 °C (DSC). The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO. The $M_w = 53,900$; the $M_n = 28,100$; and the $M_w/M_n = 1.92$ (GPC in THF).

Example 68:

Co-poly- $\{[N,N'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-bis-(L-leucine)-1,6-hexylene diester}]_{0.80}\text{-}[N^{\alpha},N^{\epsilon}\text{-(3-oxapentylene-1,5-dioxydicarbonyl)-L-lysine n-dodecyl ester}]_{0.20}\}$

25 Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ and R^3 is $-(\text{CH}_2)_6-$ (55.1128 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-dodecyl ester (Formula (IV) where R^9
30 is $-\text{CH}-$ and R^{10} is $-\text{C}(\text{O})-\text{O}-\text{C}_{12}\text{H}_{25}$) (13.1786 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III) where X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$ and

R^8 is $-(CH_2)_2-O-(CH_2)_2-$ (43.633 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 89 % and the $\eta_{red.} = 0.47$ dL/g. The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Example 69:

Co-poly- $\{[N,N'-(3\text{-oxapentylene-1,5-dioxydicarbonyl})\text{-bis-(L-leucine)-1,6-hexylene diester}]_{0.80}\text{-}[N^{\alpha},N^{\epsilon}\text{-(3-oxapentylene-1,5-dioxydicarbonyl)-L-lysine n-hexadecyl ester}]_{0.20}\}$

Dry triethylamine (30.8 ml, 0.22 moles) is added to a mixture of a di-p-toluenesulfonic acid salt of a bis-(L-leucine)-1,6-hexylene diester (Formula (Ia) where R^1 and R^2 are both $-CH_2CH(CH_3)_2$ and R^3 is $-(CH_2)_6-$ (55.1128 g, 0.08 moles); a di-p-toluenesulfonic acid salt of a L-lysine n-hexadecyl ester (Formula (IV) where R^9 is $-CH-$ and R^{10} is $-C(O)-O-C_{16}H_{33}$) (14.3008 g, 0.02 moles) (total amount of the salts is 0.1 moles); and an active bis-carbonate (Formula (III) where X is $-O-C_6H_4-NO_2$ and R^8 is $-(CH_2)_2-O-(CH_2)_2-$ (43.633 g, 0.1 moles) in dry DMF (52.5 ml) (total volume of DMF and Et_3N is 83.3 ml) at room temperature.

The temperature of the reaction mixture is increased to about 90 °C and stirred for about 12 hours. The reaction product is then cooled to room temperature, cast as a thin film onto the smooth surface, and washed with water. The polymeric product obtained thereby is dried at 30 to 40 °C under reduced pressure. The resulting polymer product is extracted with ethylacetate or butylacetate at room temperature. After purification, until a negative test result for p-nitrophenol and p-toluenesulfonic acid is received, the yield is 90 % and the $\eta_{red.} = 0.40$ dL/g. The copolymer is soluble in chloroform, THF, DMF, DMA, and DMSO.

Properties of PEAs and PEURs:Solubility and Molecular Weight Characteristics

The polymers of the present invention, as noted above, are soluble in organic solvents like chloroform, DMF, DMA, DMSO, and most of them in THF. They have a Mw in the range of about 5,000 to about 400,000 daltons. In another embodiment, the polymers according to Formula (C) have a Mw of about 10,000 to about 200,000 daltons, even about 20,000 to about 100,000 daltons. In one embodiment, the polymers of the present invention have a narrow polydispersity – Mw/Mn equals 1.0 to about 2.0, even about 1.25 to about 1.9, or even 1.5 to about 1.8.

Thermal Properties

The polymers of the present invention possess low glass transition temperatures (T_g = about 5 °C to about 60 °C). The glass transition temperature of the polymers of the present invention is determined using a Perkin-Elmer DSC-7 under a nitrogen gas flow. Due to the hydrophilic nature of some PEAs such samples should be heated prior to determining a PEAs glass transition temperature to remove any absorbed water, then cooled, and reheated again at a heating/cooling rate of 20 °C/min. The thermal data from the second DSC scan should be used in such cases.

Additionally, η_{red} for the polymers of the present invention can be determined in *m*-cresol at a concentration of 0.5 g/dL at 25 °C.

Mechanical Properties

The polymers of the present invention exhibit a wide range of mechanical properties depending on the composition the monomers used therein to produce the polymers. For example, the homopoly(ester amide)s – poly-[N,N'-sebacoyl-bis-(L-phenylalanine)-1,6-hexylene diester] and poly-[N,N'-adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] show an elongation at break of 5 - 10% and 4 - 6%, respectively. After modification of this polymer according to Examples 13 to 18 (See Table 1) and Examples 27 to 29 (See Table 2) the elongation at break increases. In one embodiment, the higher the leucine content in the copolymer, the higher the elongation at break.

TABLE 1

	Polymer	Tensile Strength (kg/cm ²)	Elongation at Break (%)
	Poly-[N,N'-sebacoyl-bis-(L-phenylalanine)-1,6-hexylene diester]	415 ± 23	7.5 ± 2.5
5	<u>Example 13:</u> Co-poly-{{[N,N'-sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.90} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.10} }	338 ± 32	15 ± 5
10	<u>Example 14:</u> Co-poly-{{[N,N'-sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.80} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.20} }	325 ± 17	72 ± 12
15	<u>Example 15:</u> Co-poly-{{[N,N'-sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.60} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.40} }	223 ± 19	105 ± 6
20	<u>Example 16:</u> Co-poly-{{[N,N'-sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.40} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.60} }	213 ± 26	152 ± 14
25	<u>Example 17:</u> Co-poly-{{[N,N'-sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.20} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.80} }	184 ± 17	189 ± 22
30	<u>Example 18:</u> Co-poly-{{[N,N'-sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.10} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.90} }	162 ± 21	193 ± 19
	Poly-N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]	139 ± 28	215 ± 38

TABLE 2

Polymer	Tensile Strength (kg/cm ²)	Elongation at Break (%)
Poly-[N,N'-adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester]	658 ± 23	5 ± 1
5 <u>Example 27:</u> Co-poly-{{[N,N'-adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] _{0.80} -[N ^α ,N ^ε -adipoyl-L-lysine n-octyl ester] _{0.20} }	480 ± 28	25 ± 4
10 <u>Example 28:</u> Co-poly-{{[N,N'-adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] _{0.60} -[N ^α ,N ^ε -adipoyl-L-lysine n-octyl ester] _{0.40} }	388 ± 22	66 ± 14
15 <u>Example 29:</u> Co-poly-{{[N,N'-adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] _{0.40} -[N ^α ,N ^ε -adipoyl-L-lysine n-octyl ester] _{0.60} }	266 ± 19	95 ± 16

Hydrophobic/hydrophilic properties

For this comparison the polymeric products described in Examples 13 to 18 and Examples 37 to 40 are used. The polymeric products are generally formed in films which are placed in water at 37 °C, removed after about 24 hours, dried with filter paper and weighed. For Examples 13 to 18, the polymers with a high content of phenylalanine in their backbones (i.e. containing a lot of lateral benzyl groups) reveal high hydrophobicity. Hydrophobicity of the polymers decreases and hydrophilicity increases with decreasing benzyl groups content and with increasing fatty lateral groups (e.g., leucine) content in the macro chains, as is shown in Table 3 below.

For Examples 37 to 40, the homopolymers based on leucine reveal relatively high hydrophilicity. Hydrophilicity of the polymers decreases and hydrophobicity increases with increase of hydrophobic fatty lateral groups content in the macro-chains, as is shown below in Table 4.

TABLE 3

	Polymer	Water Uptake (Weight %)
	Poly-N,N'-sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]	3 - 5
5	<u>Example 13:</u> Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.90} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.10}	5 - 6
10	<u>Example 14:</u> Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.80} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.20}	8 - 10
15	<u>Example 15:</u> Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.60} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.40}	13 - 15
	<u>Example 16:</u> Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.40} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.60}	16 - 18
20	<u>Example 17:</u> Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.20} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.80}	18 - 20
25	<u>Example 18:</u> Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.10} -[N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.90}	20 - 22
	Poly-N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]	20 - 24

TABLE 4

Polymer	Water Uptake (Weight %)
Poly-N,N'-sebacoyl-[bis-(L-leucine)-1,6-hexylene diester]	20 - 24
<u>Example 37:</u> Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-leucine)-1,6-hexylene diester] $\}_{0.90}$ - $[N^{\alpha},N^{\epsilon}$ -sebacoyl-L-lysine n-octyl ester] $\}_{0.10}$	12 ± 4
<u>Example 38:</u> Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-leucine)-1,6-hexylene diester] $\}_{0.80}$ - $[N^{\alpha},N^{\epsilon}$ -sebacoyl-L-lysine n-octyl ester] $\}_{0.20}$	10 ± 4
<u>Example 39:</u> Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-leucine)-1,6-hexylene diester] $\}_{0.60}$ - $[N^{\alpha},N^{\epsilon}$ -sebacoyl-L-lysine n-octyl ester] $\}_{0.40}$	6 ± 2
<u>Example 40:</u> Co-poly- $\{[N,N'$ -sebacoyl-bis-(L-leucine)-1,6-hexylene diester] $\}_{0.40}$ - $[N^{\alpha},N^{\epsilon}$ -sebacoyl-L-lysine n-octyl ester] $\}_{0.60}$	5 ± 2

In Vitro Biodegradation:

In vitro biodegradation studies are performed by weight loss. Standard films with $d = 4$ cm and $m = 450$ to 550 mg (cast onto Teflon® backings as described below) are placed into the glass vessels containing about 10 ml of 0.2 M phosphate buffer solution with a pH of about 7.4 (either pure buffer or buffer containing 4 mg of an enzyme – α -chymotrypsin or lipase) and are exposed to a temperature of about 37 °C. The films which are impregnated with enzymes are exposed to pure buffer. The films are removed from the solutions after a predetermined amount time (normally about 24 hours), dried with filter paper and weighed. The buffer or enzyme solution in the buffer is changed every 24 hours. The biodegradation study is conducted for about 120 hours (about 5 days). The biodegradation rate is assessed in mg of weight loss per cm^2 of the film surface in hours ($\text{mg}/(\text{cm}^2 \cdot \text{h})$).

The preparation of the samples for this study are produced as follows. A given amount of polymer is dissolved in chloroform (about 1 g in 10 ml) and Teflon® films ($d = 4$ cm and thickness 1 - 2 mm) are submerged into this solution, removed

and the chloroform evaporated to dryness. This procedure is repeated until the weight of the polymer on the Teflon® backing reaches about 450 to about 550 mg.

For preparing the films impregnated with enzymes, the desired enzyme (2 to 10 mg of enzyme per 1 g of polymer) is added to the polymer solution as a fine powder and then the films are prepared by sinking Teflon® films into the enzyme/polymer mixture described above.

This technique can also be used to produce medicated wound coverings with a variety of additives (i.e., enzymes, antibiotics, pain killers, cancer drugs, etc.).

The incorporation of various α -amino acids' residues into polymeric backbones can impart biodegradation to polymers which normally reveal low tendency to biodegradation. For example, a homopoly(ester amide) based on isoleucine and valine reveals a low tendency to α -chymotrypsin catalyzed biodegradation. After the incorporation of phenylalanine residues into the polymeric backbone the biodegradation rate increases, as is shown below in Table 5 with regard to Examples 3 to 6.

TABLE 5

Polymer	α -Chymotrypsin Catalyzed Biodegradation Rate (mg/cm ² • h)
Poly-N,N'-adipoyl-[bis-(L-valine)-1,4-butylene diester]	1.4×10^{-4}
Poly-N,N'-sebacoyl-[bis-(L-valine)-1,6-hexylene diester]	2.3×10^{-4}
5 <u>Example 3:</u> Co-poly- $\{[N,N'$ -adipoyl-[bis-(L-phenylalanine)-1,4-butylene diester]] _{0.80} -[N,N'-adipoyl-[bis-(L-valine)-1,4-butylene diester]] _{0.20} $\}$	8.1×10^{-4}
10 <u>Example 4:</u> Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.80} -[N,N'-sebacoyl-[bis-(L-valine)-1,6-hexylene diester]] _{0.20} $\}$	16.4×10^{-4}
15 <u>Example 5:</u> Co-poly- $\{[N,N'$ -sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]] _{0.80} -[N,N'-sebacoyl-[bis-(L-isoleucine)-1,4-butylene diester]] _{0.20} $\}$	12.5×10^{-4}
20 <u>Example 6:</u> Co-poly- $\{[N,N'$ -adipoyl-[bis-(L-phenylalanine)-1,4-butylene diester]] _{0.80} -[N,N'-adipoyl-[bis-(L-isoleucine)-1,6-hexylene diester]] _{0.20} $\}$	7.4×10^{-4}
Poly-N,N'-adipoyl-[bis-(L-phenylalanine)-1,4-butylene diester]	10.2×10^{-4}
Poly-N,N'-sebacoyl-[bis-(L-phenylalanine)-1,6-hexylene diester]	19.6×10^{-4}

25 The content of the impregnated enzyme (enzyme loading) permits regulation
 of a wide range of biodegradation rates as is shown below for lipase in Table 6.

TABLE 6

Polymer	Impregnated Lipase in mg per 1 g of Polymer	Biodegradation Rate (mg/cm ² • h)
Example 8: Co-poly- $\{[N,N'$ -adipoyl-[bis-(L-phenylalanine)-1,4-butylene diester]] _{0.80} - [N,N'-adipoyl-[bis-(L-leucine)-1,6-hexylene diester]] _{0.20} $\}$	0	0
	2	1.6×10^{-2}
	4	3.3×10^{-2}
	6	4.5×10^{-2}
	8	5.6×10^{-2}
	10	7.2×10^{-2}

With regard to Examples 26 to 28, the copolymers show an tendency to lipase catalyzed biodegradation similar to that of the corresponding homopolymer, as it is shown below in Table 7.

TABLE 7

Polymer	α -Chymotrypsin Catalyzed Biodegradation Rate (mg/cm ² • h)
Poly-[N,N'-adipoyl-[bis-L-phenylalanine)-1,6-hexylene diester]	$(7.5 \pm 0.2) \times 10^{-2}$
Example 26: Co-poly- $\{[N,N'$ -adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] _{0.90} -[N ^{α} ,N ^{ϵ} -adipoyl-L-lysine n-octyl ester] _{0.10} $\}$	7.2×10^{-2}
Example 27: Co-poly- $\{[N,N'$ -adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] _{0.80} -[N ^{α} ,N ^{ϵ} -adipoyl-L-lysine n-octyl ester] _{0.20} $\}$	6.5×10^{-2}
Example 28: Co-poly- $\{[N,N'$ -adipoyl-bis-(L-phenylalanine)-1,6-hexylene diester] _{0.60} -[N ^{α} ,N ^{ϵ} -adipoyl-L-lysine n-octyl ester] _{0.40} $\}$	6.3×10^{-2}

One manner in which films can be produced from the any of the polymer compositions described herein for biodegradation studies is discussed below.

The polymers of the present invention can be used to form, for example, medicated wound coverings using the following process. A solution of any polymer according to the present invention is formed by dissolving the desired polymer into a suitable solvent (e.g., chloroform, THF, DMF, DMA, DMSO, ethanol, etc.) and Teflon® films (d = 4 cm and thickness 1 - 2 mm) are submerged into this solution, removed and the solvent evaporated to dryness. This procedure is repeated until the weight of the polymer on the Teflon® backing reaches about 450 to about 550 mg.

For preparing the films impregnated with enzymes, a desire amount of any suitable additive (e.g., about 2 to about 10 mg of enzyme per about 1 g of polymer) is added to the polymer solution in any suitable form (e.g., a powder, liquid, solid, gas, etc.) and then the films are prepared by sinking Teflon® films into the additive/polymer mixture described above. Such additives include, but are not limited to, enzymes, antibiotics, pain killers, cancer drugs, amino acids and anesthetics.

As is discussed above, the polymers of the present invention can be used for a wide variety of applications. Such applications include, but are not limited to, sutures, scaffolds (be they medical or otherwise), ligating clips and staples, surgical tubes or catheters, orthopedic implants, barriers to prevent tissue adhesion, vascular grafts, stent coatings (medicated or non-medicated), artificial skin (medicated or non-medicated), bone substitutes, self-reinforced composites, temporary templates for cell growth, temporary contraceptives (e.g., stoppers for closing a fallopian tube, etc.), tampons, biodegradable time release patches (e.g., patches for use with one or more drugs, physiologically active substances and bactericides), artificial glands for releasing bio-active peptides and/or proteins, biodegradable packaging (for agricultural, food service, or any other packaging use), and biodegradable polymer protection films for use in protecting articles from a wide range of environmental factors (e.g., corrosion protection, water damage protection, etc.)

Films made from the polymers of the present invention can have additives added thereto to impart certain characteristics to the films. Such additives include, but are not limited to, any and all additives which may impart such polymers films with one or more anti-static, anti-mildew and/or anti-corrosion properties. For example, a volatile corrosion inhibitor could be added to a polymer film produced from one or polymers according to the present invention. Any suitable corrosion inhibitor can be used. United States Patent Nos. 4,290,912; 5,320,778; and 5,855,975 disclose vapor phase or volatile corrosion inhibitors and are incorporated herein by reference in their entirety for their teachings of such compounds.

As noted above, the polymer compositions of the present invention can be used to form controlled release devices. Such devices allow for the controlled release of a desired compound and/or compounds over an extended period of time.

A wound covering produced using a polymer composition according to the present invention is detailed in Figure 1– 3. Figure 1 shows a cross-sectional view of a wound covering **100** made in accordance with the above method using a polymer **102** according to the present invention and four additives therein (i.e., a bacteriophage **104**, an antibiotic **106**, an anesthetic **108**, and an enzyme **110**). It should be noted that although a specific combination of additive is discussed above, any suitable combination of additives can be used depending upon the final use intended for the polymer product.

The wound covering **100** of Figure 1 utilizes can optionally include a support film made of Teflon® (or any other suitable support film). Alternatively, it is also possible to forego the use of a support film (such as Teflon®) and form a film from the solution of biodegradable polymer and any additives added thereto.

Figure 2 depicts a process for making a biodegradable polymer film for use as a wound covering using at least one polymer according to the present invention which does not require the use of a support film. The polymer films according to the method of Figure 2 are produced by dissolving one or more polymer composition according to the present invention in a suitable organic solvent and, optionally, adding to the solution **101** any desired additives. Next, the solution is, for example, cast into a thin film by pouring a polymer solution (which may or may not contain

additives therein) into, for example, a suitable mold and removing the solvent therefrom by any suitable method (e.g., by evaporation, heating, etc.). If a support layer is utilized, then the support layer can be submerged into the solution of polymer and, optionally, additive(s), and allowing the support layer to dry.

5 The wound covering **100** of Figures **1–3** may be perforated with suitable sized holes **120** to provide breathability and to allow the migration of gases such as water vapor. The holes **120** formed in the wound covering **100** can be any suitable size so long as they serve to not only allow air to pass through the wound covering and reach the wound, but also allow gases such as water vapor to pass through the wound
10 covering in either direction.

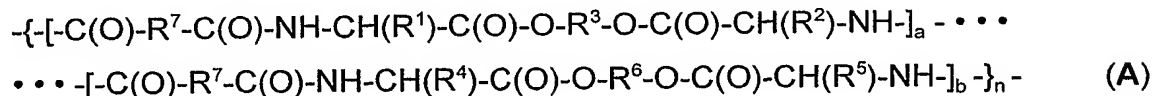
 Although the invention has been shown and described with respect to certain embodiments, equivalent alterations and modifications would be apparent to others skilled in the art upon the reading and understanding of this specification. In particular with regard to the various functions performed by the above described
15 components, the terms used to describe such components are intended to correspond, unless otherwise indicated, to any component which performs the specified function of the described component (e.g., that is functionally equivalent), even though not structurally equivalent to the disclosed structure which performs the function in the herein illustrated exemplary embodiments of the invention. In
20 addition, while a particular feature of the invention may have been disclosed with respect to only one of several embodiments, such feature may be combined with one or more other features of the other embodiments as may be desired and advantageous for any given or particular application.

CLAIMS

What is claimed is:

1. A co-poly(ester amide) composition which contains at least two amino acid sub-components comprising:

5 repeating units according to the following formula:



10 where R^1 , R^2 , R^4 and R^5 are independently selected from $-CH_3$, $-CH_2CH_3$, linear and branched C_3 to C_{20} alkyl, C_2 to C_3 thioalkyl, linear or branched C_4 to C_{20} thioalkyl, $-CH_2-C_6H_5$, $-CH_2-CH_2-C_6H_5$, and linear and branched C_3 - C_{20} alkyl with at least one terminal phenyl group; R^3 and R^6 are independently selected from $-(CH_2)_x-$, where x is from 2 to about 40; R^7 is selected from $-(CH_2)_y-$, where y is from 2 to about 40; n is from about 10 to about 1,000; the ratio of a/b is in the range of about 90:10 to about 10:90; and at least one of R^1 , R^2 , R^3 or the first R^7 is different from at
15 least one of R^4 , R^5 , R^6 or the second R^7 .

2. The composition of claim 1, wherein the at least two amino acid sub-components are identical.

3. The composition of claim 1, wherein the at least two amino acid sub-components are different.

20 4. The composition of claim 1, wherein the ratio of a/b is about 80:20 to about 20:80.

5. The composition of claim 1, wherein the ratio of a/b is about 60:40 to about 40:60.

6. The composition of claim 1, wherein n is about 20 to about 500.

7. The composition of claim 1, wherein n is about 30 to 300.

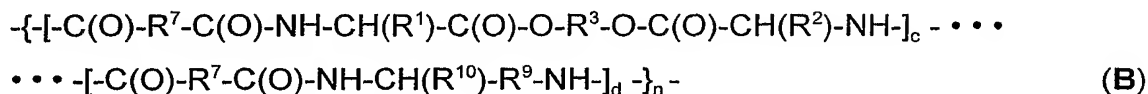
8. The composition of claim 1, wherein R^1 , R^2 , R^4 and R^5 are independently selected from $-CH_3$, $-CH_2CH_3$, linear and branched C_3 to C_6 alkyl, $-CH_2-CH_2-S-CH_3$, and $-CH_2-C_6H_5$.

9. The composition of claim 1, wherein R^3 and R^6 are independently selected from $-(CH_2)_x-$, where x is from 2 to about 12.

10. The composition of claim 1, wherein R^7 is selected from $-(CH_2)_y-$, where y is from 2 to about 20.

11. A co-poly(ester amide) composition which contains at least two amino acid sub-components comprising:

repeating units according to the following formula:



where R^1 and R^2 are independently selected from $-CH_3$, $-CH_2CH_3$, linear and branched C_3 to C_{20} alkyl, C_2 to C_3 thioalkyl, linear or branched C_4 to C_{20} thioalkyl, $-CH_2-C_6H_5$, $-CH_2-CH_2-C_6H_5$, and linear and branched C_3 - C_{20} alkyl with at least one terminal phenyl group; R^3 is selected from $-(CH_2)_x-$, where x is from 2 to about 40; R^7 is independently selected from $-(CH_2)_y-$, where y is from 2 to about 40; R^9 is selected from $-(CH_2)_r-$, where r is from 1 to about 40; R^{10} is selected from $-C(O)-O-C_mH_{2m+1}$ where m is 1 to about 60, and $-C(O)-O-R''$ where R'' is selected from hydrogen, $CH_2-C_6H_5$, $-CH_2-CH_2-C_6H_5$, linear and branched C_3 - C_{20} alkyl with at least one terminal phenyl group; n is about 10 to about 1,000; and the ratio of c/d is in the range of about 80:20 to about 20:80.

12. The composition of claim 11, wherein the at least two amino acid sub-components are identical.

13. The composition of claim 11, wherein the at least two amino acid sub-components are different.

5 14. The composition of claim 11, wherein the first R⁷ is identical to the second R⁷.

15. The composition of claim 11, wherein the first R⁷ group is different than the second R⁷ group.

10 16. The composition of claim 11, wherein the ratio of c/d is about 70:30 to about 30:70.

17. The composition of claim 11, wherein the ratio of c/d is about 60:40 to about 40:60.

18. The composition of claim 11, wherein n is about 20 to about 500.

19. The composition of claim 11, wherein n is about 30 to 300.

15 20. The composition of claim 11, wherein R¹ and R² are independently selected from -CH₃, -CH₂CH₃, linear and branched C₃ to C₆ alkyl, -CH₂-CH₂-S-CH₃, and -CH₂-C₆H₅.

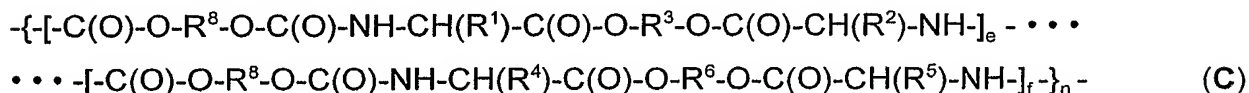
21. The composition of claim 11, wherein R³ is selected from -(CH₂)_x-, where x is from 2 to about 12.

20 22. The composition of claim 11, wherein R⁹ is selected from -(CH₂)_r-, where r is 4.

23. The composition of claim 11, wherein R" is selected from hydrogen, -CH₂-C₆H₅, and -C(O)-O-C_mH_{2m+1}, where m is 1 to about 40.

24. A co-poly(ester urethane) composition which contains at least two amino acid sub-components comprising:

5 repeating units according to the following formula:



10 where R¹, R², R⁴ and R⁵ are independently selected from -CH₃, -CH₂CH₃, linear and branched C₃ to C₂₀ alkyl, C₂ to C₃ thioalkyl, linear or branched C₄ to C₂₀ thioalkyl, -CH₂-C₆H₅, -CH₂-CH₂-C₆H₅, and linear and branched C₃-C₂₀ alkyl with at least one terminal phenyl group; R³ and R⁶ are independently selected from -(CH₂)_x-, where x is from 2 to about 40; R⁸ is selected from -(CH₂)_z-, where z is from 2 to about 40, and -(CH₂)_j-O-(CH₂)_k-, where j and k are independently selected from 1 to about 20; n is about 10 to about 1,000; and the ratio of e/f is in the range of about 15 90:10 to about 10:90; and at least one of R¹, R², R³ or the first R⁸ is different from at least one of R⁴, R⁵, R⁶ or the second R⁸.

25. The composition of claim 24, wherein the at least two amino acid sub-components are identical.

20 26. The composition of claim 24, wherein the at least two amino acid sub-components are different.

27. The composition of claim 24, wherein the ratio of e/f is about 80:20 to about 20:80.

28. The composition of claim 24, wherein the ratio of e/f is about 60:40 to about 40:60.

29. The composition of claim 24, wherein n is about 20 to about 500.

30. The composition of claim 24, wherein n is about 30 to 300.

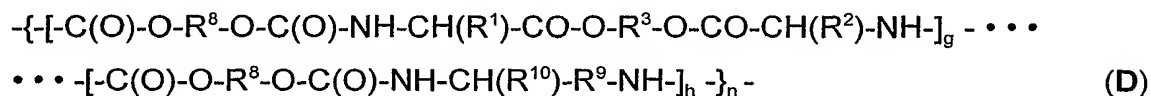
31. The composition of claim 24, wherein R¹, R², R⁴ and R⁵ are independently selected from -CH₃, -CH₂CH₃, linear and branched C₃ to C₆ alkyl, -CH₂-CH₂-S-CH₃, and -CH₂-C₆H₅.

32. The composition of claim 24, wherein R³ and R⁶ are independently selected from -(CH₂)_x-, where x is from 2 to about 12.

33. The composition of claim 24, wherein R⁸ is selected from -(CH₂)_z-, where z is from 2 to about 12, and -(CH₂)₂-O-(CH₂)₂-.

34. A co-poly(ester urethane) composition which contains at least two amino acid sub-components comprising:

repeating units according to the following formula:



where R¹ and R² are independently selected from -CH₃, -CH₂CH₃, linear and branched C₃ to C₂₀ alkyl, C₂ to C₃ thioalkyl, linear or branched C₄ to C₂₀ thioalkyl, -CH₂-C₆H₅, -CH₂-CH₂-C₆H₅, and linear and branched C₃-C₂₀ alkyl with at least one terminal phenyl group; R³ is selected from -(CH₂)_x-, where x is from 2 to about 40; each R⁸ is independently selected from -(CH₂)_z-, where z is from 2 to about 40, and -(CH₂)_j-O-(CH₂)_k-, where j and k are independently selected from 1 to about 20; R⁹ is selected from -(CH₂)_r-, where r is from 1 to about 40; R¹⁰ is selected from -C(O)-O-C_mH_{2m+1} where m is 1 to about 60, and -C(O)-O-R'' where R'' is selected from

hydrogen, $-\text{CH}_2-\text{C}_6\text{H}_5$, $-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_5$, linear and branched C_3-C_{20} alkyl with at least one terminal phenyl group; n is about 10 to about 1,000; and the ratio of g/h is in the range of about 80:20 to about 20:80.

35. The composition of claim 34, wherein the at least two amino acid sub-
5 components are identical.

36. The composition of claim 34, wherein the at least two amino acid sub-
components are different.

37. The composition of claim 34, wherein the first R^8 is identical to the
second R^8 .

10 38. The composition of claim 34, wherein the first R^8 group is different than
the second R^8 group.

39. The composition of claim 34, wherein the ratio of g/h is about 70:30 to
about 30:70.

15 40. The composition of claim 34, wherein the ratio of g/h is about 60:40 to
about 40:60.

41. The composition of claim 34, wherein n is about 20 to about 500.

42. The composition of claim 34, wherein n is about 30 to 300.

20 43. The composition of claim 34, wherein R^1 and R^2 are independently
selected from $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, linear and branched C_3 to C_6 alkyl, $-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_3$,
and $-\text{CH}_2-\text{C}_6\text{H}_5$.

44. The composition of claim 34, wherein R^3 is selected from $-(CH_2)_x-$, where x is from 2 to about 12.

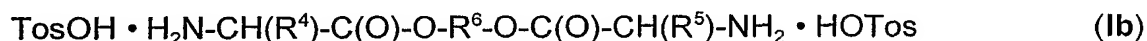
45. The composition of claim 34, wherein R^9 is selected from $-(CH_2)_r-$, where r is 4.

5 46. The composition of claim 34, wherein R'' is selected from hydrogen, $-CH_2-C_6H_5$, and $-C(O)-O-C_mH_{2m+1}$, where m is 1 to about 40.

47. The composition of claim 34, wherein R^8 is selected from $-(CH_2)_z-$, where z is from 2 to about 12, and $-(CH_2)_2-O-(CH_2)_2-$.

10 48. A method for producing biodegradable polymers comprising the steps of:

(A) combining at least one di-p-toluenesulfonic acid salt of a bis-(α -amino acid) α,ω -alkylene diesters according to Formulas (Ia) and/or (Ib) and optionally at least one di-p-toluenesulfonic acid salt of an ester according to Formula (IV) with at least one active diester according to Formula (II) or at least one active bis-carbonate of a diol according to Formula (III):



where R^1 , R^2 , R^4 and R^5 are independently selected from $-CH_3$, $-CH_2CH_3$, linear and branched C_3 to C_{20} alkyl, C_2 to C_3 thioalkyl, linear or branched C_4 to C_{20} thioalkyl, $-CH_2-C_6H_5$, $-CH_2-CH_2-C_6H_5$, and linear and branched C_3 - C_{20} alkyl with at least one terminal phenyl group; R^3 and R^6 are independently selected from $-(CH_2)_x-$, where x is from 2 to about 40; R^7 is selected from $-(CH_2)_y-$, where y is from 2 to

25

about 40; X is $-\text{O}-\text{C}_6\text{H}_4-\text{NO}_2$; R^8 is selected from $-(\text{CH}_2)_z-$, where z is from 2 to about 40, and $-(\text{CH}_2)_j-\text{O}-(\text{CH}_2)_k-$, where j and k are independently selected from 1 to about 20; R^9 is selected from $-(\text{CH}_2)_r-$, where r is from 1 to about 40; and R^{10} is selected from $-\text{C}(\text{O})-\text{O}-\text{C}_m\text{H}_{2m+1}$, where m is 1 to about 60, and $-\text{C}(\text{O})-\text{O}-\text{R}''$ where R'' is selected from hydrogen, $-\text{CH}_2-\text{C}_6\text{H}_5$, $-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_5$, linear and branched C_3-C_{20} alkyl with at least one terminal phenyl group;

(B) adding a tertiary amine initiator to the mixture of (A);

(C) mixing the mixture of (B) at room temperature while increasing the temperature of the mixture to a temperature in the range of about 60 °C to about 120 °C;

(D) subjecting the mixture of (B) to mixing at the final temperature of (C) for about 8 to about 16 hours; and

(E) separating the polymer from the reaction by-products to yield a polymer product.

49. The method of claim 48, wherein the final temperature for step (C) is about 85 °C to about 95 °C and the time for step (D) is about 11 to about 13 hours.

50. The method of claim 48, wherein the combination in step (A) is one diester according to Formula (Ia), one diester according to Formula (Ib) and one active diester according to Formula (II), wherein at least one of R^1 , R^2 or R^3 is different from at least one of R^4 , R^5 or R^6 .

51. The method of claim 48, wherein the combination in step (A) is one diester according to Formula (Ia) or (Ib) and two active diesters according to Formula (II), wherein the R^7 groups in the active diesters according to Formula (II) are different.

52. The method of claim 48, wherein the combination in step (A) is one diester according to Formula (Ia) or (Ib), one diester according to Formula (IV) and one active diester according to Formula (II).

53. The method of claim 48, wherein the combination in step (A) is one diester according to Formula (Ia), one diester according to Formula (Ib) and one active bis-carbonate according to Formula (III), wherein at least one of R¹, R² or R³ is different from at least one of R⁴, R⁵ or R⁶.

5 54. The method of claim 48, wherein the combination in step (A) is one diester according to Formula (Ia) or (Ib) and two active bis-carbonates according to Formula (III), wherein the R⁸ groups in the active diesters according to Formula (III) are different.

10 55. The method of claim 48, wherein the combination in step (A) is one diester according to Formula (Ia) or (Ib), one diester according to Formula (IV) and one active bis-carbonate according to Formula (III).

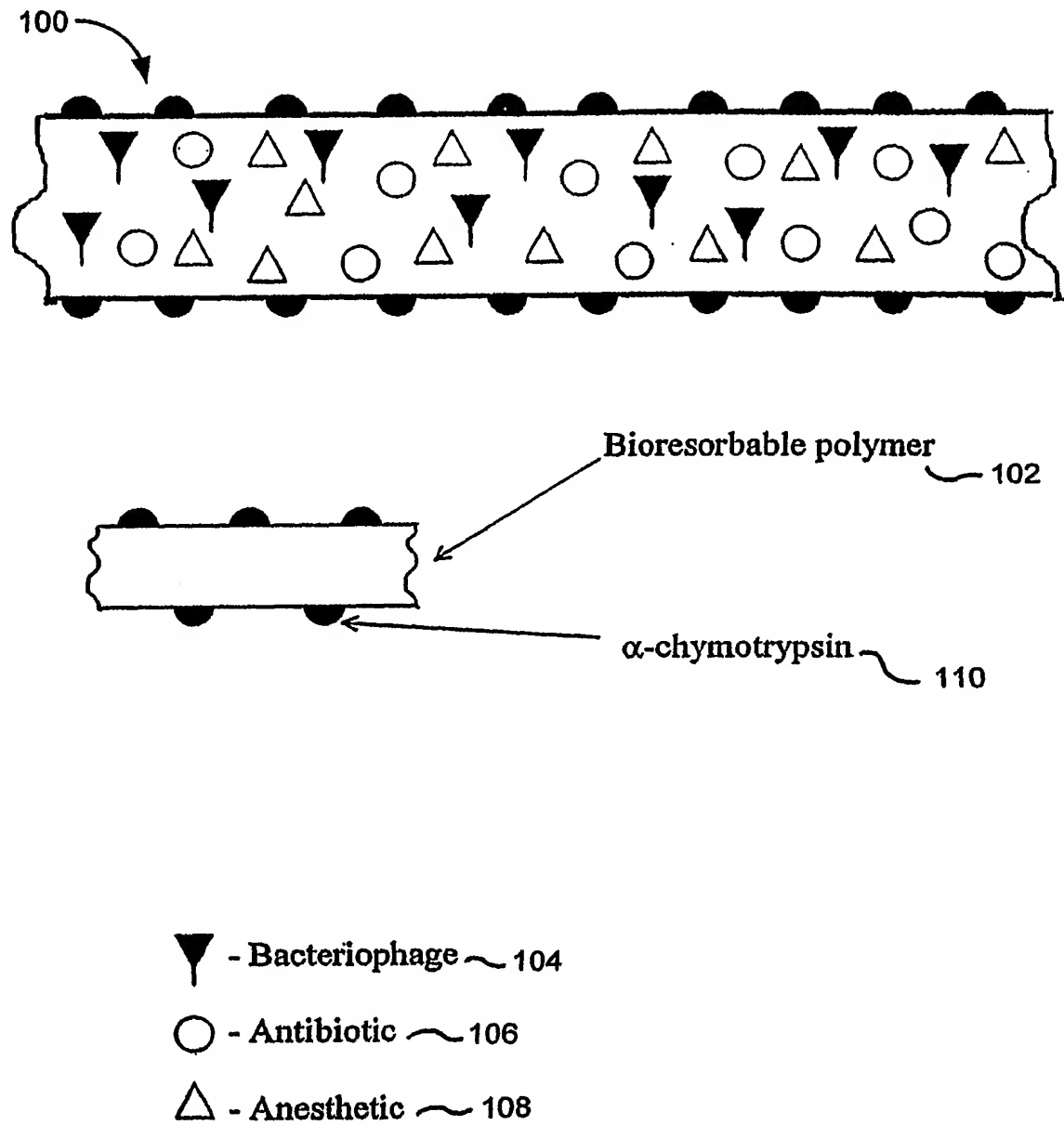
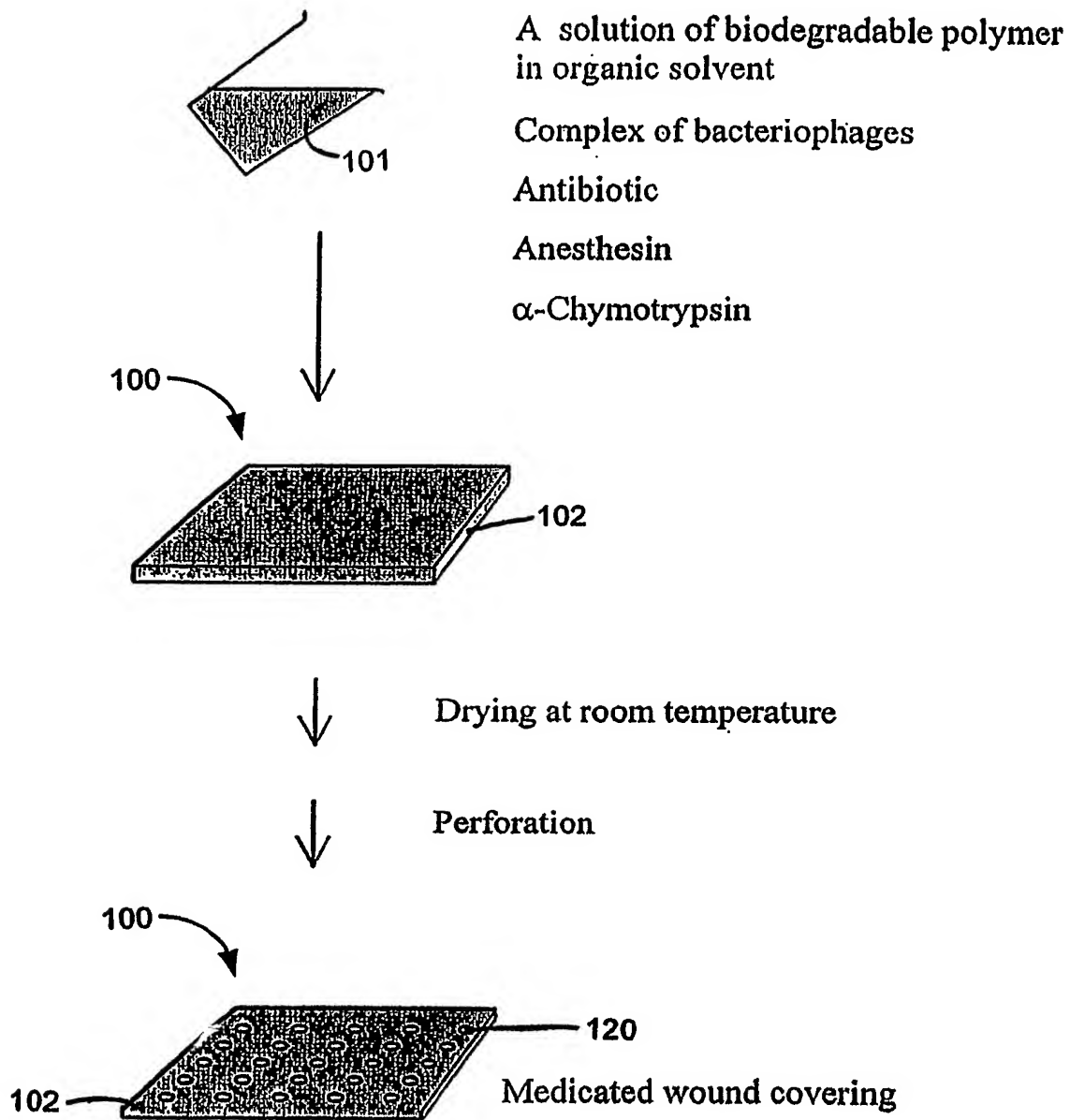
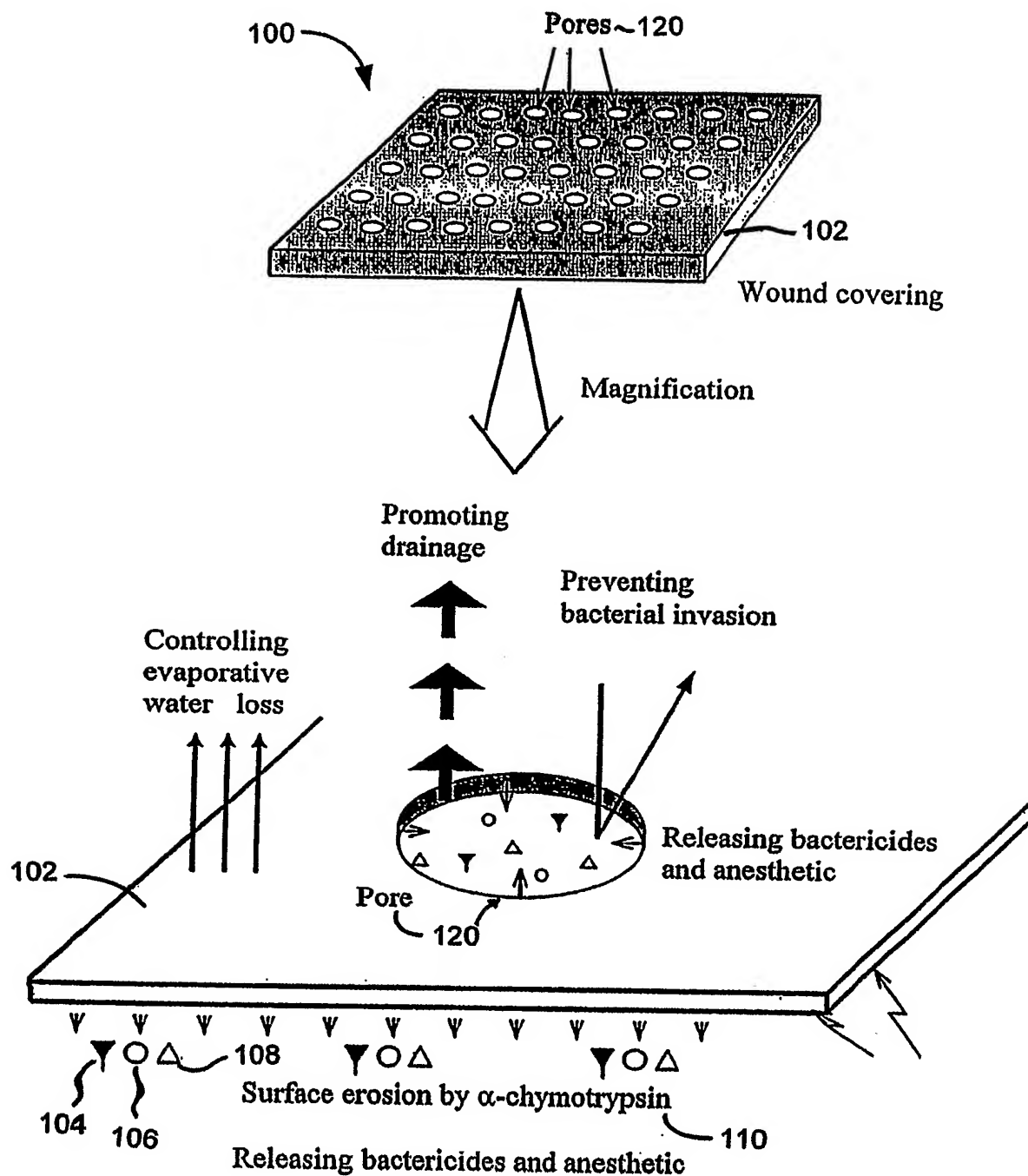


Figure 1

**Figure 2**

**Figure 3**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/01258

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : C08G 63/00, 63/02; C08G 73/00; A61F 2/00; US CL : Please See Extra Sheet. According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 528/170, 176, 184, 196, 271, 272, 295, 302; 523/113, 115, 124; Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched None Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Please See Extra Sheet.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,002,171 A (TAFT) 11 January 1977, see entire document.	1-55
A	US 4,273,890 A (HIRZY) 16 July 1981, see entire document.	1-55
A	US 4,281,077 A (HIRZY) 28 July 1981 see entire document.	1-55
A	US 5,295,985 A (ROMESSER et al) 22 March 1994 see entire document.	1-55
A	US 5,630,972 A (PATNODE et al) 20 May 1997 see entire document.	1-55
A	US 6,160,084A (LANGER et al) 12 December 2000 see entire document.	1-55
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 17 JUNE 2002		Date of mailing of the international search report 11 JUL 2002
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer PATRICIA HIGHTOWER Telephone No. (703) 308-0661 Jean Proctor Paralegal Specialist

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/01258

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

528/170, 176, 184, 196, 271, 272, 295, 302;

523/113, 115, 124;

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

EAST 1.3: copolyesteramide or copolyesterurethane or (biodegradable or degradable) or disposable or absorbent or polyaminoacids or (biscarbonate or diol or polyol or alcohol) or toluenesulfonic acid or (artificial or medical or surgical or pharmaceutical or sanitary)